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THE USE OF COMPRESSED OXYGEN IN ELEMENTARY ORGANIC ANALYSIS AND OF SODA-LIME IN THE QUANTITATIVE DETERMINATION OF CARBON DIOXIDE.

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THE ordinary method of elementary organic analysis in which use is made of air and oxygen contained in a gasometer, suffices where but few determinations are to be made. The manipulation is, however, too lengthy to permit of rapid work, and having occasion to make carbon and hydrogen determinations in a large number of foods used in connection with experiments with a respiration calorimeter in this laboratory, it was necessary to modify materially the method so as to increase its rapidity. The method formerly employed is essentially the same as that described in most text-books on organic analysis, and may be briefly outlined as follows:

Oxygen obtained by heating a mixture of potassium chlorate and manganese dioxide was collected over water in a Mitscherlich gasometer. It was then freed from carbon dioxide, and dried

as it entered the combustion tube. The substance was burned in the usual manner in a tube filled with granular copper oxide. The resulting water was collected in a tube containing glass wool drenched with sulphuric acid, and the carbon dioxide was absorbed in a potash bulb, which was followed by a small sulphuric-acid tube to collect the water coming over from the potash solution. On the end of a series of absorption tubes, a small U-tube was placed containing fused calcium chloride to absorb the moisture of the air in case of back suction. After the substance was completely burned and oxygen had been passed through, the tube was swept out with a current of air to remove all oxygen from the system.

There are several disadvantages in obtaining oxygen by the above method. The time consumed in generating and collecting the gas is considerable. Impurities present in manganese dioxide cause the formation of some carbon dioxide, which mixes with the oxygen and necessitates special care in purifying the gas before use. The oxygen standing in the gasometer over water becomes saturated with aqueous vapor. In order to remove all traces of carbon dioxide and water vapor it is necessary to pass the oxygen through the purifying apparatus very slowly. Furthermore, owing to the large quantities of these impurities present, the materials used in purification, *i. e.*, potassium hydroxide and sulphuric acid respectively, require frequent replenishing.

The use of Pepys or Mitscherlich gasometers for holding oxygen is an almost universal practice. These gasometers, if constructed of metal, soon leak owing to the attacks of acid fumes and vapors always present in a laboratory, and are constantly needing repairs. Glass gasometers do away with the large mass of metal, but rely on metallic pipes, cocks and connections to receive and deliver the gas. These connections are equally liable to the attack of acid, resulting in leakage and consequent loss of gas. The fragile nature of such gasometers and the necessity for transportation to the sink when being filled, make their handling difficult. Finally, the original cost of such an apparatus is not inconsiderable.

To overcome these disadvantages use is made of compressed oxygen in steel cylinders. Progress in the compressed air

industry has reached such a point that it is comparatively easy to secure a strong, thoroughly well-tested cylinder of highly compressed oxygen. These cylinders are made in all sizes, containing from a few gallons to 100 cubic feet of oxygen. For the laboratory, a cylinder containing ten cubic feet or seventy-five gallons is of convenient size. The oxygen thus compressed is of a high degree of purity. Formerly hydrocarbons were used to lubricate the machinery for compressing the gas, thereby causing contamination of the oxygen with volatile hydrocarbons, which introduced serious errors when the gas was used in elementary analysis. Manufacturers have, however, replaced the lubricating oils with graphite, thereby eliminating the undesirable impurities of gaseous hydrocarbons. In the several cylinders of oxygen tested in this laboratory, gaseous hydrocarbons, or at least any hydrocarbons, not completely absorbed by the sulphuric acid of the drying apparatus to be described beyond, were never detected.[1]

The oxygen in these steel cylinders is comparatively dry and free from carbon dioxide, so that its purification is easy to accomplish. The carbon dioxide is absorbed by soda-lime in a small U-tube.[2] Owing to the small quantity of carbon dioxide present, one tube of this sort will remove this impurity completely for over twenty-five combustions. The soda-lime tube is followed by the drying apparatus, consisting of a cylinder about twelve cm. high half filled with concentrated sulphuric acid, through which the oxygen bubbles, thereby indicating the rate of flow.

[1] Oxygen compressed in this form was first used in this laboratory for making combustions with an Atwater-Blakeslee bomb-calorimeter. These bomb-calorimeters have been introduced into several laboratories, all of which, consequently, have a supply of compressed oxygen. For those laboratories not possessing a cylinder the following is appended: The price of a ten-foot cylinder is about ten dollars. The so-called "commercial" oxygen, which differs from the "medical" only in so far as it has been, perhaps, a little less thoroughly washed and purified, costs at the rate of ten cents per foot; *i. e.*, one dollar per ten cubic feet. This amount is not great compared with the cost of an ordinary Mitscherlich or Pepys gasometer. Inasmuch as the gasometers are used almost exclusively to hold oxygen, it will be seen that they are not indispensable to the ordinary laboratory supplied with a cylinder of oxygen. Ten cubic feet will last for a great many carbon and hydrogen combustions, while the advantage of using a cylinder of this gas in the lecture-room is obvious.

The writers would here express their obligations to Mr. A. K. Johnston of the S. S. White Dental Manufacturing Company, Princess Bay, N. Y., who has furnished much valuable information.

[2] This and all other U-tubes here mentioned were five inches long and five-eighths inch outside diameter, as this was found to be the most convenient size.

Following this is a small U-tube containing pumice stone drenched with sulphuric acid to retain any moisture, which may escape absorption. The cylinder usually absorbs all the moisture, so that no gain in weight of the U-tube is observed. When the oxygen is run at an abnormally rapid rate, the U-tube shows a slight gain, as was proved by an experiment in which the U-tube gained one and eight-tenths milligrams after the oxygen had been passing rapidly through the system for thirty minutes.

Inasmuch as the oxygen contained in the steel cylinders is under great pressure, some method of regulating the flow of gas, as it enters the combustion tube, must be devised. The expensive precision and reduction valves used ordinarily with these cylinders can be replaced by the following simple arrangement: A rubber tube leading from the cylinder connects with a T-tube, one end of which dips one inch under mercury in a small bottle fitted with a rubber stopper having two holes. The second hole is left open. A rubber tube connects the other end of the T-tube with the purifying apparatus, which is in turn connected by rubber tubing to the combustion tube. This last rubber tube is supplied with a pinch-cock. When the valve on the oxygen cylinder is opened slightly, the gas will flow out, and passing through the driers produce a bubbling in the sulphuric-acid cylinders. As yet no gas escapes through the mercury. If now, as is often the case, one wishes to regulate the flow of gas, the pinch-cock is closed until the desired rate of flow is secured. Any excess of gas now escapes through the mercury trap. It is always possible to adjust the valve on the oxygen cylinder finally, so as to prevent any appreciable loss of oxygen through the mercury.

The furnaces used are of the ordinary Bunsen pattern, and have twenty-six burners. A hard glass combustion tube was filled in the usual manner with granular copper oxide. The oxidized copper spirals used to fill the entrance end of the tube after introducing the substance to be burned, were made by winding moderately stout copper wire in layers around a glass rod until the desired size was obtained. Such spirals were found to be more durable than those made from copper gauze. Red antimony rubber stoppers were found to possess a marked superiority in withstanding heat over those of ordinary rubber, and they were, accordingly, used

at each end of the combustion tube. All rubber connections were made with $\frac{5}{32}$-inch red antimony tubing.

The water formed during the process of combustion was absorbed as usual in a Volhard U-tube containing glass wool drenched with sulphuric acid. The absorption of the carbon dioxide was effected by passing the gas after leaving the sulphuric acid U-tube through a U-tube filled with specially prepared soda-lime, followed by a similar U-tube containing, in one limb, soda-lime, and in the other fused calcium chloride. This substitution of soda-lime for the usual absorbent of carbon dioxide, *i. e.*, potassium hydroxide, while by no means new,[1] has given such satisfactory results in our hands as to warrant publication.

Repeated tests of a most exacting nature have shown that soda-lime, prepared as described below, absorbs carbon dioxide more completely and rapidly than potassium hydroxide solution. Passing 150 liters of air containing three and five-tenths grams of carbon dioxide through a system of two soda-lime U-tubes and a final check U-tube containing glass beads drenched with barium hydroxide solution gave no turbidity in the last tube. The air was aspirated at the rate of 500 cc. per minute.[2] In another experiment[3] ordinary air from the room was drawn through one soda-lime U-tube, followed by a Drechsel gas-washing cylinder containing a strong barium hydroxide solution, at the rate of 2100 cc. per minute without noting any turbidity in the barium hydroxide solution. It is needless to add that these tests could in no way be duplicated, if potassium hydroxide solution were used. Obviously then, so far as the absorption of the carbon dioxide is concerned, there need be practically no limit to the rate at which the gas may be passed though the soda-lime tubes. As a matter of fact, in this method the rate of flow is regulated solely by the completeness of combustion. In case of back suction there was no liquid to look out for as when a potash solution was used. To prevent atmospheric moisture from being

[1] See *Ann. Chem.* (Liebig), **285**, 385.

[2] Preliminary Investigations on the Metabolism of Nitrogen and Carbon in the Human Organism, by W. O. Atwater, C. D. Woods, and F. G. Benedict. Bulletin 44, Office of Experiment Stations, U. S. Department of Agriculture, p. 28.

[3] This Journal, **20**, 299.

absorbed when back suction occurred, a small sulphuric-acid tube completed the series of tubes.

As dry air passes through the carbon dioxide absorbent in any system of tubes, it carries with it varying quantities of moisture, which must be collected and weighed to secure the true weight of the absorbed carbon dioxide. Actual experiments show this amount of water lost from a soda-lime tube during a combustion to be on the average about one-fourth of that lost from an ordinary Geissler potash bulb. To collect this water from the soda-lime tube, one limb of a second U-tube is filled with calcium chloride, while the other is filled with soda-lime. The limb filled with soda-lime is connected with the first U-tube. Both tubes are weighed. In ordinary combustions the second tube rarely gains as much as two milligrams, while a sulphuric-acid tube following a potash bulb ordinarily gains from six to ten milligrams. To prove the complete retention of water by the calcium chloride, a sulphuric-acid U-tube was placed immediately following, and weighed before and after a combustion, and in no case was any gain in weight observed. An additional advantage of this second U-tube lay in the fact that the first tube could be completely used up without the fear that carbon dioxide might escape absorption. When the second tube gained much more than two milligrams, it was an indication that the first tube was exhausted, and it was accordingly replaced by a fresh tube. A fresh soda-lime tube can be used ordinarily for six combustions before becoming exhausted, while it is hardly safe to use a potash bulb more than twice.

The progress of the absorption of carbon dioxide by the soda-lime is also indicated by a marked change in color. The fresh soda-lime has a slightly yellowish tinge, while the portion converted to carbonate is pure white. With a potash solution no such indication is present, and one must rely solely on the increase in weight of the potash bulb. As the carbon dioxide is absorbed in one limb of the tube, a very marked line of advancement is noticed where the color change occurs. This line advances as the absorption proceeds, and the efficiency of any tube can be immediately ascertained by noting this change in color.

A not inconsiderable item in considering the relative merits of

soda-lime and potassium hydroxide solution is the question of the expense of the potash bulbs. Compared with the U-tubes they are very expensive, and their fragile nature is a decided disadvantage. Where a large number of combustions are to be made, it has been found advantageous to have a number of these soda-lime U-tubes filled in advance, and fitted with one-holed rubber stoppers carrying small bent glass tubes plugged at the ends with short bits of rubber tubing and a piece of glass rod. These tubes can be weighed to the second decimal place and, when wanted, checked up accurately on the balance.

In order to still further shorten the time of making a combustion, sweeping out the oxygen with air after combustion was omitted. As the tubes were weighed originally filled with air, the oxygen filling them after combustion, should be replaced by air. This is accomplished after the tubes have been disconnected in the following manner: Air, purified by passing through a soda-lime U-tube and a sulphuric-acid U-tube, is drawn by gentle suction with the mouth through the tubes to be weighed. These air-purifying tubes are kept in readiness, so that very little time is consumed in the process. If the tubes were weighed filled with oxygen, the error would be almost inappreciable, since the empty space in the U-tubes is small, particularly as compared with the empty space in a potash bulb. Before each weighing, the tubes were wiped off lightly with a piece of cheese-cloth. Weighings were in each case made with a counterpoise. The ease with which a U-tube can be wiped, as compared with a potash bulb, is apparent.

It was found that time could be saved by using two furnaces. One person then gave all his time to watching the furnaces, while another person made the weighings and kept the tubes replenished. By thus utilizing about one-third of the time of a second man, an average of two combustions an hour could be made. The furnaces were both connected with the same oxygen cylinder by inserting a T-tube just beyond the mercury safety trap previously described. Each furnace was supplied with an independent set of drying and purifying tubes. This was necessary in order to observe the rate of flow of each current of gas. To test the efficiency of the apparatus and method, substances of known composition and purity, *i. e.*, cane-sugar

and benzoic acid, were analyzed and the results are given in the following table:

Substance.	Amount used. Gram.	Carbon dioxide found. Gram.	Carbon Found. Per cent.	Carbon Theor. Per cent.	Water found. Gram.	Hydrogen Found. Per cent.	Hydrogen Theor. Per cent.
Cane-sugar..	0.2000	0.3075	41.94	42.10	0.1145	6.41	6.43
" " ..	0.2018	0.3111	42.05	....	0.1158	6.42	....
Benzoic acid	0.2058	0.5193	68.83	68.85	0.0911	4.95	4.92
" "	0.1738	0.4388	68.87	....	0.0780	5.02	....

The cane-sugar was obtained as rock-candy. This was dried, powdered, and dried again until there was no loss in weight. The benzoic acid was a chemically pure preparation of the market. It was melted and recrystallized twice before being used. No traces of moisture could then be found.

The above results, fair samples of many others, seemed to justify the use of this method for determining carbon and hydrogen in organic substances. As a direct application of this method, it will suffice to say that over eighty samples of foods have been burned, and the agreement of duplicates is, to say the least, remarkable. Agreement as close as 0.03 or 0.04 per cent. was often obtained. Obviously this agreement substantiates in no way the absolute determination of carbon and hydrogen, but it does imply that the method is easy and regular, presenting no great difficulties in manipulation.

One essential feature is the soda-lime. As ordinarily prepared and sold in the market, it is a mixture of sodium and calcium hydroxides fused and granulated. Its chief use has been as a drier for gases and for determining organic nitrogen. Such soda-lime has very little absorptive power for carbon dioxide. To absorb carbon dioxide readily the soda-lime must be moist. This moisture is best obtained by modifying the method of preparation. One kilogram of commercial caustic soda, "Greenbank Lye," is treated with 500–600 cc. water in an iron kettle forming a strong solution, or more properly a thin paste. While still hot, one kilogram of quicklime, coarsely powdered, is rapidly added, stirring constantly with an iron rod or piece of gas pipe. The lime is slaked by the water of the caustic soda solution, and soon the whole mass heats and steams up. While in this stage, it is advisable to keep the mass stirred and the lumps broken up. No outside heat is necessary, and as soon as

cool the product may be placed in wide-mouthed bottles, and the corks sealed in with paraffin or wax. When cool, it should not be moist enough to show water as such, *i. e.*, no particle should glisten in strong light. If too dry, a small quantity of water can be readily added after the soda-lime is made, though the great danger lies in adding too much water, thereby making the lime too pasty for the most efficient absorption. We have made over fifty kilograms of such soda-lime in the past three years, and invariably secure a good product when using the above formula.

While moisture is essential in securing the complete absorption of carbon dioxide, the amount of moisture carried away from a soda-lime U-tube by an air current is, as has before been stated, much less than that brought away from a potash bulb. Assuming that the soda-lime here used is a mixture of the hydroxides of sodium and calcium, and that the normal carbonates are formed when carbon dioxide is absorbed, we could properly have two equations; *viz.*,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Thus one molecule of carbon dioxide absorbed liberates one molecule of water from the hydroxides. Accordingly, for every gram of carbon dioxide absorbed about four-tenths gram of water is liberated. In actual experimenting, however, but a very small portion of this water leaves the soda-lime U-tube. In one tube 2.7467 grams of carbon dioxide were absorbed and only 0.1378 gram of water left the soda-lime tube. The sodium carbonate formed appears to retain the major portion of the water hygroscopically. While the deca-hydrated sodium carbonate loses its water of crystallization readily, the anhydrous salt takes up water with great avidity, and it is to this that we must attribute the retention of so much water in the soda-lime tube. Were it possible to form the acid carbonates of sodium and calcium under these conditions, the water would be retained chemically, and in fact not liberated. To disprove this high improbability some of the white spent soda-lime was heated in a long tube to low redness with provision for absorbing any carbon dioxide given off, exactly similar to the absorbing ap-

paratus used above in the case of combustions. The first soda-lime U-tube lost one and eight-tenths milligrams, while the second containing also calcium chloride gained one and six-tenths milligrams, which shows that no carbon dioxide was driven out of the spent soda-lime. A large amount of water was, however, given off, indicating that the white seemingly dry carbonate had really absorbed considerable water hygroscopically. The whitening in a tube is not, therefore, due to drying out. Experiment has also shown that moistening white, spent soda-lime does not increase its absorbent power for carbon dioxide.

Soda-lime prepared as outlined above is recommended as a general reagent for freeing gases from carbon dioxide, such as normal air in determining gas densities. As a reagent for the quantitative determination of carbon dioxide, both in elementary organic analysis and in air analyses, it has given excellent satisfaction. The air analyses were made in connection with the respiration calorimeter above referred to. It appears to be an excellent general substitute for potassium hydroxide solution in all cases where the solid form of reagent is not proscribed.

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THE DETERMINATION OF CARBON MONOXIDE, METHANE, AND HYDROGEN BY COMBUSTION.

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IN the development of technical gas analysis the researches of Winkler, Hempel, Lunge, and others have given us many methods which are both rapid and exact and which yield results quite as satisfactory as those obtained by the classical methods of Bunsen. But for the determination of hydrogen and methane modern methods have been found to be far from satisfactory. The combustion of hydrogen and hydrocarbons by means of copper oxide is no longer used because of its inconvenience. The combustion of hydrogen by means of palladium asbestos is open to the error which may result from the partial burning of the methane present. The fractional combustion of hydrogen by palladium sponge and the absorption of hydrogen by palladium

black are exact, but the palladium needs to be frequently removed from the tube and heated, to render it again active. The last three of these methods, moreover, leave the methane still to be determined, a detail which so prolongs the analysis as to exclude the methods from general adoption.

It was but natural that gas analysts should prefer to use some method by which both hydrogen and methane could be simultaneously determined, and the procedure which is now most frequently employed is the Hempel explosion method or some modification of it. In speed and convenience of manipulation this method leaves little to be desired. Unfortunately, however, the results are neither constant nor accurate, first because of the smallness of the gas volume which is exploded, any error being thus multiplied about eightfold, and second because of the danger of the formation of oxides of nitrogen. This last difficulty is largely avoided if the determination is carried out as Hempel directs, but in the employment of an explosion pipette in which the gases are confined between two glass stop-cocks, there is no way of judging of the violence of the explosion. This is a point of considerable importance, for if the explosion is too violent the formation of oxides of nitrogen is probable, while if too weak the combustion is liable to be incomplete. If the explosion is made with oxygen instead of air the danger of formation of oxides of nitrogen from the nitrogen originally present in the gas mixture is increased[1] and the violence of the explosion becomes so great that Gill, who recommends this procedure, divides the explosion into two parts, using half of the required oxygen in each.

It seemed necessary, therefore, in seeking to improve the procedure for the determination of hydrogen and methane, to devise some method which would permit of the use of large volumes of gas and would so diminish the violence of the union of oxygen and the combustible gases as to reduce to a minimum the possibility of injury to the operator, and the probability of the formation of oxides of nitrogen. It was apparent that to attain these ends it would be necessary to abandon the method of explosion and to replace it by some form of slow combustion. The gris-

[1] See the researches of Bunsen and Hempel upon this point.

oumeter devised by Winkler seemed to be an apparatus which might be adapted to this purpose provided that it were found possible to attain complete combustion without mixing the combustible gases and the oxygen *before*[1] their introduction into the grisoumeter. This proved to be feasible.

The determination of carbon monoxide by absorption with cuprous chloride offers many difficulties. The absorbent is somewhat difficult to prepare and keep, and the absorption can be completed in a reasonable time only by using two solutions of cuprous chloride and bringing the gas and the reagent into intimate contact by vigorous shaking.[2] Vignon[3] and later Noyes and Shepard[4] have avoided this absorption of carbon monoxide by exploding the gas simultaneously with the hydrogen and methane and then determining the contraction, the volume of carbon dioxide formed, and the oxygen consumed in the explosion. As will be seen below this procedure can also be carried out with satisfactory results by means of the combustion method which is here described.

The apparatus used for the combustion of the various gases is quite similar to the "grisoumeter" described by Winkler[5] and was made from a Hempel simple gas pipette for solid and liquid reagents[6] by cutting off the upper bulb and attaching in its place, by means of a rubber tube, a level bulb like that used by Hempel in his explosion pipette.[7] Through the opening of the single-hole rubber stopper *a* there passes a glass tube *b* which is open at both ends and contains an iron wire *c* three mm. in diameter. Another iron wire *m* of about one and five-tenths mm. diameter is pushed through the stopper and is then wound several times around the glass tube and cut off at the same height as the larger wire. This arrangement of the conducting wires is preferable to that suggested by Winkler, since the relative positions of the wires remain unchanged when the stopper

[1] Mixing the oxygen and combustible gases before passing them into the grisoumeter was not attempted, for the combustion has been known to pass back through the capillary and explode the main mixture with most deplorable results.

[2] See Dennis and Edgar: This Journal, **19**, 859.

[3] *Bull. Soc. Chim.*, *1897*, p. 832.

[4] This JOURNAL, **20**, 343.

[5] *Ztschr. anal. Chem.*, **28**, 288; Hempel: Methods of Gas Analysis, p. 236.

[6] Hempel: Methods of Gas Analysis, p. 35, Fig. 21, *b*.

[7] *Ibid.*, p. 103, Fig. 44.

is pushed into place and, as will be seen later, the use of a cement of any sort is avoided. The upper ends of the iron wires are connected by a platinum spiral *d*, contact between the platinum and iron being effected by simply wrapping the platinum wire several times around the iron wires. The platinum wire is one-fourth mm. in diameter and the coil into which it is bent is about two mm. in diameter and contains from twenty to thirty turns. After the spiral has been attached to the iron wires it is bent into the form of a horizontal S. Below the rubber stopper the smaller iron wire is fastened directly to the double binding-post P. The opening between the large iron wire and the tube through which it passes is closed air-tight by means of a piece of small rubber tubing carefully wired in place. The lower end of the iron wire is connected, by means of a binding-screw *e* and a piece of suitable wire, to the second binding-post P_2. Both binding-posts P_1 and P_2 should be insulated from the iron stand.

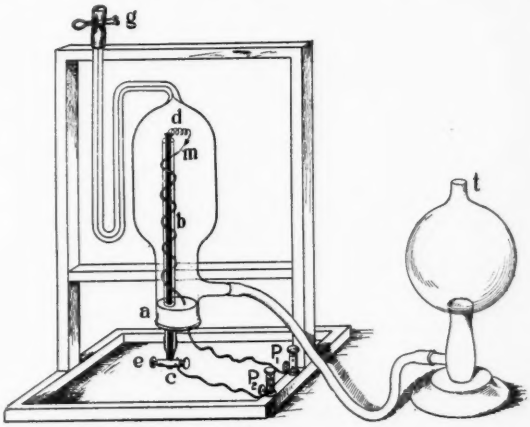


Fig. 1.

After the rubber stopper carrying the spiral has been inserted in place and the iron wires have been connected with the binding-posts, the pipette and capillary are filled with mercury by raising the level-bulb, the pinch-cock *g* on the rubber tube on the capillary is closed, and suction is applied to the tube *t* of

the level-bulb by means of a water suction-pump. The air contained in the glass tube *b* is thus removed and the tube remains completely filled with mercury.

The gas volumes were measured in a simple Hempel burette[1] provided with a water-jacket (see Fig. 2). Mercury was used as the confining liquid and a drop of water was introduced into the

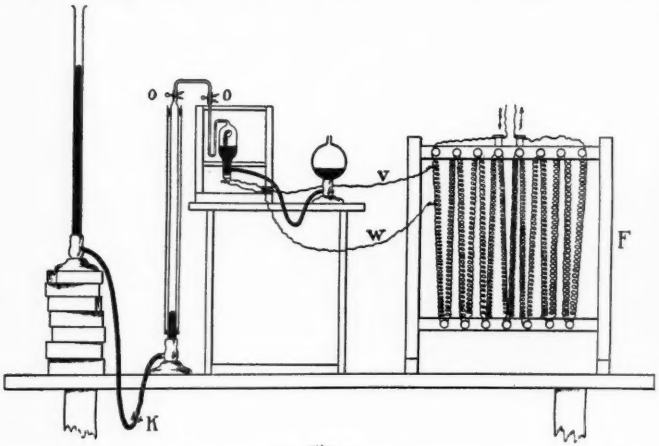


Fig. 2.

burette to insure the complete saturation of the gases with moisture.

The method of procedure which was finally adopted for the combustion of the gases is as follows:

The combustion pipette is first completely filled with mercury by raising the level-bulb, and a measured quantity of the gas to be burned is then introduced. A quantity of oxygen more than sufficient to completely burn the gas is drawn into the gas burette and its volume noted. The burette is then connected with the pipette by the usual bent capillary tube (see Fig. 2) and the level-bulb of the pipette and the level-tube of the burette are placed at such heights that the gases in both pipette and burette are approximately under atmospheric pressure. A screw pinch-cock *k* which has previously been placed upon the rubber tube joining the burette with its level-tube is now tightly screwed down so as to prevent, for the present, any movement of the mer-

[1] Hempel: Methods of Gas Analysis, p 22. Fig. 17.

cury in the burette. The level-tube is now placed at such a height that when the screw pinch-cock *k* is opened the mercury will rise to the top of the burette but will not pass over into the pipette. The pinch-cocks *o*,*o* on the connections between the burette and pipette are now opened and the electric current, which should be just strong enough to maintain the spiral at a red heat, is turned on. Any electrical apparatus furnishing a current of sufficient strength to heat the platinum spiral to redness may, of course, be employed. If the current from a dynamo or storage battery is at the operator's disposal, the arrangement shown in Fig. 2. can be recommended as being both simple and convenient. The current is passed through the resistance frame F. (We have used a small frame carrying German silver wire about one and five-tenths mm. in diameter.) The terminals on the combustion pipette are connected with the frame by means of the flexible wires *V* and *W*, the ends of these wires being simply hooked into the coiled wire of the frame. The current passing through the platinum spiral can then be varied at will by simply hooking the end of *W* into the resistance coil at a greater or less distance from *V*.

When the spiral has been brought to the proper temperature the screw pinch-cock *k* is carefully opened and a slow and steady current of oxygen is passed over into the pipette. From ten to twenty cc. of oxygen per minute may be introduced, but the amount is, of course, somewhat dependent upon the length and temperature of the spiral. The combustion takes place quietly without the appearance of a flame and if the operation is properly conducted there is no possibility of an explosion since the combustible gas and the oxygen are in separate vessels and are made to combine as fast as they mix. Nevertheless a screen of heavy glass is always placed between the pipette and the operator to insure protection for the face in case of possible accident.[1] After the oxygen has been passed into the pipette, the spiral is kept at a red heat for about one minute to insure complete combustion of the gas. When, however, hydrogen alone is being burned, the combustion is complete almost as soon as sufficient oxygen has been introduced. When the combustion is finished

[1] This precaution is invariably taken in this laboratory in all combustion or explosion analyses of gas mixtures.

the residual gas is passed back into the burette and measured.

The volume of gas which may be taken for the combustion is limited only by the capacity of the measuring burette, but for convenience in handling neither the combustible gas, the oxygen required, nor the residue after combustion is allowed to exceed 100 cc. The volume of gas in the pipette at any time during the combustion should be sufficient to prevent the mercury from rising and covering the spiral, or short-circuiting the current. This would take place if pure hydrogen were burned by adding pure oxygen, but the difficulty in this case is avoided by introducing into the 100 cc. of hydrogen about 95 cc. of a mixture of equal parts of oxygen and air.

In the following tables are given the results obtained with this apparatus in the determination of hydrogen and carbon monoxide and in the analysis of the residue of illuminating gas both before and after the removal by absorption of carbon monoxide. No corrections were made for the slight changes in temperature and barometric pressure which may have taken place during the progress of any one determination.

HYDROGEN.

The hydrogen was made by allowing hydrochloric acid to act upon zinc[1], the vapors of the acid being removed by shaking the gas with a strong solution of potassium hydroxide.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.	VI. cc.	VII. cc.	VIII. cc.	IX.[2] cc.	X.[2] cc.
Hydrogen taken	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15	35.0	34.75
Oxygen and air added	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95	100.0	100.0
Total	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10	135.0	134.75
Residue after combustion	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4	82.65	82.75
Contraction	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7	52.35	52.00
Equivalent to hydrogen	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13	34.9	34.67
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Hydrogen found	99.9	99.9	99.9	99.7	99.9	99.9	99.9	100.0	99.7	99.8

CARBON MONOXIDE.

This was prepared by heating together oxalic and sulphuric

[1] Cf. Cooke and Richards: *Am. Chem. J.*, (*1888*), 10, 100.

[2] In IX and X air alone was added, and smaller amounts of hydrogen were taken. The results are fairly good but are not as satisfactory as those obtained with oxygen and air.

acids and removing the carbon dioxide with potassium hydroxide. Duplicate volumetric analyses by absorption with cuprous chloride showed the gas to be 99.7 per cent. pure.

The oxygen which was used in these and the other combustions was made from potassium chlorate and manganese dioxide and was purified by being shaken with a solution of potassium hydroxide. Absorption by alkaline pyrogallol showed it to be very nearly pure, 99.9 per cent.

Two volumes of carbon monoxide unite with one volume of oxygen to form two volumes of carbon dioxide. Hence the volume of the carbon monoxide taken is equal either to the volume of carbon dioxide which is formed, or to twice the contraction resulting from the combustion. In the following tabulation of results the percentages of carbon monoxide obtained in both ways are given. There are also added the percentage results calculated on the assumption that the gas contained only 99.7 per cent. of carbon monoxide as indicated by the absorption with cuprous chloride.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.	VI. cc.	VII. cc.	VIII. cc.
Carbon monoxide taken	73.1	60.7	82.1	80.95	78.1	77.95	83.05	79.0
Oxygen taken	50.7	49.65	52.2	49.8	50.55	50.8	52.4	50.4
Total	123.8	110.35	134.3	130.75	128.65	128.75	135.45	129.4
Residue after combustion	87.4	80.1	93.3	90.4	89.65	89.8	93.95	89.95
Contraction	36.4	30.25	41.0	40.35	39.0	38.95	41.50	39.45
Residue after absorbing CO_2 in KOH pipette	14.5	19.5	11.5	9.6	11.7	12.05	11.05	11.25
Carbon dioxide	72.9	60.6	81.8	80.8	77.95	77.75	82.90	78.70
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
CO, calculated from contraction	99.6	99.7	99.9	99.7	99.9	99.9	99.9	99.9
CO, calculated from CO_2 formed	99.7	99.8	99.6	99.8	99.8	99.7	99.8	99.6
CO, from contraction, assuming gas to be 99.7 per cent. pure	99.9	100.0	100.2	100.0	100.2	100.2	100.2	100.2
CO, from CO_2, assuming gas to be 99.7 per cent. pure	100.0	100.1	99.9	100.1	100.1	100.0	100.1	99.9

METHANE.

Methane was first prepared from zinc dust and chloroform in aqueous alcohol, as proposed by Sabanejeff[1] and recommended by Phillips.[2] The product was, however, very unsatisfactory as

[1] *Ber. d. chem. Ges.*, 9, 1810.
[2] *Am. Chem. J.*, 16, 172.

it contained not only vapors of alcohol and chloroform but also a considerable amount of hydrogen. Methane was then made from sodium acetate and soda-lime and the hydrogen which is simultaneously formed was removed by passing the gas over palladium black. Four determinations, by this method, of the hydrogen present gave the following results:

	I. cc.	II. cc.	III. cc.	IV. cc.
Gas taken	99.2	100.0	99.55	99.2
Residue after passage over palladium black	92.75	93.5	93.0	92.8
Hydrogen	6.45	6.5	6.55	6.4
	Per cent.	Per cent.	Per cent.	Per ct.
Hydrogen	6.5	6.5	6.6	6.5

It was to be expected that the residue from the hydrogen determinations would be pure methane, but when 40.75 cc. of this gas was burned with oxygen in the combustion pipette the contraction amounted to 81.65 cc. and 42.5 cc. of carbon dioxide was formed, thus plainly indicating the presence of a gas or vapor with more than one carbon atom in the molecule. The gas was therefore not of sufficient purity to give trustworthy data concerning the accuracy of the combustion method when used for methane alone, and unfortunately there was not sufficient time at our disposal to permit of further experiments upon the preparation of pure methane. In order, however, to obtain, in an indirect way at least, some idea as to the accuracy of the method in the determination of methane, a series of combustions was made of the residue from illuminating gas after the removal of the absorbable gases.

SIMULTANEOUS COMBUSTION AND DETERMINATION OF HYDROGEN AND METHANE.

Illuminating gas was passed into fuming sulphuric acid to remove hydrocarbon vapors and heavy hydrocarbons, then shaken with alkaline pyrogallol to remove oxygen, carbon dioxide, and the fumes of the sulphuric acid, and finally shaken first with old and then with fresh cuprous chloride to remove carbon monoxide. Measured portions of the residue which now contained hydrogen, methane, and nitrogen were then introduced into the combustion pipette and burned with oxygen in the manner described above.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.
Gas residue taken	61.4	64.5	67.0	64.0	65.7
Oxygen taken	98.5	96.55	98.55	97.6	100.0
Total	159.9	161.05	165.55	161.6	165.7
Residue after combustion	58.8	54.95	55.3	56.3	57.6
Contraction	101.1	106.1	110.25	105.3	108.1
Residue after absorbing CO_2 in KOH pipette	34.3	29.15	28.6	30.7	31.4
Carbon dioxide found	24.5	25.80	26.7	25.6	26.2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrogen	56.4	56.3	56.6	56.4	56.5
Methane	39.9	40.0	39.9	40.0	39.9
Nitrogen (diff.)	3.7	3.7	3.5	3.6	3.6

To obtain an idea of the relative accuracy and constancy in the results by the combustion and explosion methods in the hands of the same operator, two analyses of the same gas residue were carefully made with the Hempel explosion pipette, mercury being used here also as the confining liquid.

	I. cc.	II. cc.
Gas residue taken	12.0	12.35
Air added	83.2	83.45
Total	95.2	95.8
Residue after explosion	75.3	75.25
Contraction	19.9	20.55
Residue after absorbing CO_2 in KOH pipette	70.35	70.2
Carbon dioxide found	4.95	5.05
	Per cent.	Per cent.
Hydrogen	55.3	56.4
Methane	41.3	40.9
Nitrogen (diff.)	3.4	2.7

SIMULTANEOUS COMBUSTION AND DETERMINATION OF CARBON MONOXIDE, HYDROGEN, AND METHANE.

A mixture of these gases together with nitrogen was obtained by extracting from illuminating gas by means of the usual absorbents, only the hydrocarbon vapors, heavy hydrocarbons, oxygen, and carbon dioxide. A measured volume of the residue was transferred to the combustion pipette and burned with oxygen. The residual gas was then passed back into the burette, measured to ascertain the contraction, and then passed into the caustic potash pipette to absorb the carbon dioxide and again drawn

back and measured. In the meantime a known volume of hydrogen had been brought into the combustion pipette. This was then connected with the burette which now contained nitrogen and the unconsumed oxygen, the current was turned on, and the oxygen was passed over into the hydrogen. From the resulting contraction the excess of oxygen was ascertained and the difference between this and the oxygen first taken gives the amount of oxygen consumed in the combustion of the carbon monoxide, hydrogen, and methane.

Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane, and nitrogen existing in the original mixture. The reactions which take place in the combustion and the volume changes due to these reactions are the following :[1]

$$\underset{2\text{ vols.}}{2CO} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2CO_2}.$$

Contraction in burning 2 vols. CO = 1 vol.
Hence contraction for 1 vol. CO = $\frac{1}{2}$ vol.

$$\underset{2\text{ vols.}}{2H_2} + \underset{1\text{ vol.}}{O_2} = \underset{\text{liquid.}}{2H_2O}.$$

Contraction in burning 2 vols. H = 3 vols.
Hence contraction for 1 vol. H = 1.5 vols.

$$\underset{1\text{ vol.}}{CH_4} + \underset{2\text{ vols.}}{2O_2} = \underset{1\text{ vol.}}{CO_2} + \underset{\text{liquid.}}{2H_2O}.$$

Contraction in burning 1 vol. CH_4 = 2 vols.

From the above equations we have

Contraction = $\frac{1}{2}$ CO + $\frac{3}{2}$ H + $2CH_4$.
Carbon dioxide formed = CO + CH_4.
Oxygen consumed = $\frac{1}{2}$CO + $\frac{1}{2}$H + $2CH_4$.

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived. Noyes and Shepard give

(1) H = Contraction minus oxygen consumed.
(2) CO = $\frac{2}{3}$($2CO_2$ + $\frac{1}{2}$H—oxygen consumed).
(3) CH_4 = CO_2—CO.

[1] Cf. Viguon : *Bull. Soc. Chim.*, *1897*, p. 832.

(4) $N = \text{Original volume} - (H + CO + CH_4)$.

Instead of (2) and (3) we may also use

$$CO = CO_2 - CH_4.$$

$$CH_4 = \frac{2\ \text{Contraction} - CO_2 - 3H}{3}.$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, V representing the volume of the gas mixture taken for the combustion.

$$H = V - CO_2.$$

$$CO = \tfrac{1}{3}CO_2 + V - \tfrac{2}{3}\ \text{contraction}.$$

$$CH_4 = \tfrac{2}{3}CO_2 + \tfrac{2}{3}\ \text{contraction} - V.$$

	I. cc.	II. cc.	III. cc.	IV. cc.
Volume of gas residue taken	83.45	85.05	83.05	86.95
Oxygen added	97.65	96.25	97.90	99.95
Total	181.10	181.30	180.95	186.90
Volume after combustion	49.3	46.95	49.75	49.5
Contraction resulting from combustion	131.8	134.35	131.20	137.4
Volume after absorption of carbon dioxide	13.05	10.15	13.75	12.0
Volume of carbon dioxide formed in the combustion	36.25	36.80	36.0	37.5
Hydrogen taken for determination of excess of oxygen	50.65	40.8	41.35	40.9
The preceding + volume remaining after absorption CO_2	63.70	50.95	55.10	52.9
Volume after combustion	32.15	28.3	21.2	24.75
Contraction resulting from this combustion	31.55	22.65	33.9	28.15
Oxygen in excess ($\frac{1}{3}$ preceding contraction)	10.52	7.55	11.3	9.38
Oxygen consumed in combustion of CO, H, and CH_4	87.13	88.70	86.6	90.57

From the above experimental results the calculated percentages of the various gases are as follows:

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.
Carbon monoxide	6.2	6.1	6.2	6.0
Hydrogen	53.5	53.7	53.7	53.9
Methane	37.3	37.2	37.2	37.1
Nitrogen (difference)	3.0	3.0	2.9	3.0

In carrying on the various combustions by which the above results were obtained, it was observed that a much stronger current is required to maintain the spiral at a red heat in an atmosphere of gases of low molecular weight than is needed with heav-

ier gases, this being probably due to the different thermal capacities of the various gases and to the varying velocities of the different gas molecules. This phenomenon is especially marked in the combustion of hydrogen, for with this gas it is necessary to markedly decrease the strength of the current as the combustion proceeds, since otherwise a current which will heat the spiral only to redness in the atmosphere of hydrogen at the beginning, is liable to melt the platinum wire in the mixture of nitrogen and oxygen which remains after the combustion is completed.

An interesting reaction which was observed during the progress of the work is that a mixture of methane and water vapor when heated by the spiral reacts as follows :

$$CH_4 + H_2O = CO + 3H_2.^1$$

According to this equation one volume of methane should yield four volumes of the mixture of carbon monoxide and hydrogen. On actual experiment it was found that 24.1 cc. of impure methane expanded to 74.5 cc. from which cuprous chloride absorbed 16.5 cc. This 16.5 cc. of carbon monoxide shows that an equal volume of methane was present in the original gas, and according to the above equation the 16.5 cc. of methane on being heated in the presence of the water vapor, should show an increase in volume of 49.5 cc. The expansion observed was 50.4 cc., a result which is sufficiently close to sustain the above reaction. That the observed expansion does not agree more nearly with the calculated increase in volume is doubtless due to the fact that at high temperatures carbon monoxide reacts with water vapor, forming carbon dioxide and hydrogen.[2] We confirmed the accuracy of this statement by introducing into the combustion pipette 79.75 cc. of pure, moist carbon monoxide, and heating the spiral for five minutes. The volume was thereby increased to 82.75 cc. from which 3.05 cc. of carbon dioxide were absorbed by potassium hydroxide.

CORNELL UNIVERSITY, July, 1898.

[1] Several years ago Coquillion observed that the same reaction takes place in the presence of a red-hot palladium spiral.—*Compt. rend.*, **86**, 1198.

[2] Cf. Dixon : *J. Chem. Soc.*, **49**, 99, 100.

THE SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF ALKALINE CHLORIDES.

By C. E. LINEBARGER.

Received December 31 1898.

THE object of this investigation is to determine the surface-tensions of aqueous solutions of the chlorides of lithium, sodium, and potassium up to the limits of their solubility. The apparatus described in a previous number of this Journal[1] permits of the same degree of accuracy when the liquid is filled with suspended particles as when it is clear. The saturation of a liquid with a solid can accordingly be accomplished with the capillary tubes right in the mixture, and the surface-tension can be measured from time to time until the saturation is completed. The operations of determining the surface-tension of a saturated solution are as follows: The solution is saturated in a thermostat at the required temperature. A sample is then transferred to the tube of the apparatus and, the temperature being the same as before, several readings are made. Some of the powdered solid is then added and with frequent agitation readings are taken at intervals of thirty minutes or so for several hours. If the preliminary saturation has been total, these readings are the same.

The alkaline chlorides used were bought as chemically pure. Lithium chloride (Koenig's C. P.) was not subjected to further purification, but the chlorides of sodium and potassium were recrystallized a couple of times.

The solutions of potassium and of sodium chloride were prepared by weighing the well-dried salts and dissolving them in known weights of water. The solutions of lithium chloride were

[1] Vol. 18, No. 6, June, 1896. I have substituted for the compression bulb therein described the following simple arrangement. A large bottle filled with water is placed on a bench on the table so as to give an effective fall of water of about two feet. The water is siphoned over into a second bottle, the siphon-tube reaching to its bottom. This bottle is closed with a twice-perforated rubber stopper, through which pass the siphon-tube and an elbow-tube connected with the capillary tubes of the apparatus. The air forced from the second is passed through a piece of thermometer tubing to prevent too rapid a flow and a solid glass bead placed in the connecting rubber hose to act as a stop-cock. By pressing the hose around the head with the thumb and finger so as to form a channel alongside it, the flow of air can be regulated with great nicety.

made from weighed quantities of water and of a strong solution of the salt that had been analyzed for chlorine.

The specific gravities were determined with pycnometers of different styles and sizes, and are referred to water at 4°. Their accuracy is denoted by the number of decimal places retained.

The data are given in the following tables:

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF LITHIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{10}$ inch.	Surface-tension in dynes per cm.
9.18	2.28	1.05023	1.259	54.50	73.17
18.06	4.70	1.10298	1.259	55.38	78.17
26.14	7.11	1.15468	1.259	56.50	83.39
40.49	12.02	1.25904	1.259	58.23	93.88

Lithium chloride is so soluble and prone to supersaturation that the surface-tension of its saturated solution was not measured. As a hydrate and not the pure salt crystallizes from its solution, it was not thought that this datum would present anything of especial interest. The strongest solution examined was very near to saturation.

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{10}$ inch.	Surface-tension in dynes per cm.
5.62	1.04	1.0370	2.366	29.29	71.59
10.87	2.06	1.0726	2.366	28.41	73.04
13.52	2.52	1.0944	1.259	52.63	73.71
15.72	3.04	1.1123	2.366	28.11	75.04
		Temperature = 20°.			
5.62	1.04	1.0388	2.366	29.01	72.38
10.87	2.06	1.0746	2.366	28.55	73.78
15.72	3.04	1.1146	2.366	28.30	75.87
26.19[1]	5.38[1]	1.2c046	2.333	28.27	80.60

The surface-tension of a sodium chloride solution saturated at 25° was not determined. The determinations at 20° and 25° show such constant differences that its value may be calculated with no appreciable error by subtracting from the surface-tension of the solution saturated at 20° the average difference between

[1] Saturated solution.

the determinations made on the same solutions at the two temperatures, for the solubility of common salt varies very slightly with the temperature.

SURFACE-TENSIONS OF AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

Temperature = 25°.

Per cent. of salt.	Mols. of salt per liter.	Specific gravity.	Apparatus constant.	Distance between tubes in $\frac{1}{10}$ inch.	Surface-tension in dynes per cm.
9.09	1.29	1.0555	1.257	53.45	72.05
10.71	1.53	1.0665	1.278	52.26	72.33
16.67	2.48	1.1069	1.257	52.02	73.61
23.08	3.57	1.1526	1.257	51.11	75.39
26.44[1]	4.18	1.17885	1.257	50.98	76.97

The data given in the preceding tables are plotted in Figs. 1 and 2; the ordinates of both are surface-tensions, and the abscissas concentrations, expressed in the first figure as percentages, and in the second as mols. per liter.

The percentage curves show that the surface-tensions are the

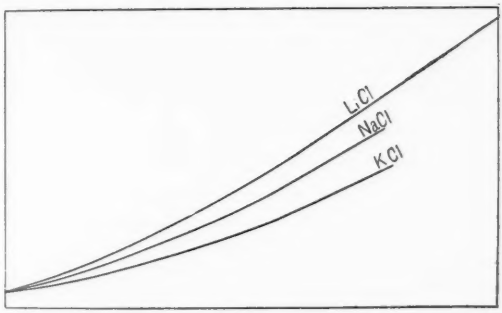


Fig. 1.

greater the smaller the molecular mass of the salt. Thus, the curve for sodium chloride lies about midway between those for lithium and potassium chloride. The surface-tension of these salt solutions is seen to be a function of their molecular masses. This is very plainly brought out by the curve in Fig. 2, where the concentrations are expressed in mols. per liter. It is seen that the surface-tensions of the solutions of the alkaline chlorides are the same, for the curve represents the behavior of each of the salts examined.

[1] Saturated solution.

As has already been found by Bulinginsk,[1] Valson,[2] Quincke,[3] Volkmann,[4] Rother,[5] Traube,[6] and Dorsey,[7] the surface-tensions of the solutions of the salts increase with the concentration. The investigators named did not use very concentrated solutions, however, and assumed that the surface-tension was a linear function of the concentration. This conclusion is not justified when the surface-tension is measured throughout the

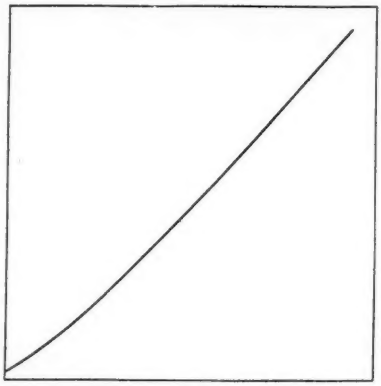


Fig. 2.

entire range of solubility of an alkaline chloride. The curve in Fig. 2 is slightly convex towards the axis of abscissas. It is, however, for small changes in concentration, practically a straight line, and for such concentration changes a formula of the form $\gamma' = \gamma + ka$ may be applied, where γ' denotes the surface-tension of the solution, γ that of water, k a constant, and a the concentration expressed in mols. per liter. At 25° the surface-tension of pure water is 69.85 dynes per cm.[8] We accordingly may establish the following equations:

Between 0 and 1 mol. $\gamma' = 69.85 + 1.48\ a$,
" 1 " 2 mols. $\gamma' = 69.85 + 1.55\ a$,
" 2 " 3 " $\gamma' = 69.85 + 1.62\ a$,
" 3 " 4 " $\gamma' = 69.85 + 1.70\ a$,
" 4 " 5 " $\gamma' = 69.85 + 1.78\ a$.

1 *Pogg. Ann.*, **134**, 440 (*1868*).
2 *Ann. chim. phys.* (4), **20**, 361 (*1870*).
3 *Pogg. Ann.*, 337 and 560 (*1877*).
4 *Wied. Ann.*, **17**, 353 (*1882*).
5 *Ibid.*, **21**, 576 (*1884*).
6 *J. prakt. Chem.*, **31**, 192 (*1885*).
7 *Phil. Mag.*, *Nov. 1897*, p. 369.
8 Ramsay and Shields: *Ztschr. phys. Chem.*, **12**, 432 (*1893*).

There are too few data to permit of establishing the values of the constant k for concentrations greater than five mols. Still since the values of the "k's" increase by about 0.08 as the concentration increases by one mol., if it be legitimate to assume that this regularity continues, similar formulas may readily be found for greater concentrations.

ESTIMATION OF THE LIME, POTASH, AND PHOSPHORIC ACID IN HAWAIIAN SOILS PROBABLY AVAILABLE FOR THE IMMEDIATE CROP.

By Walter Maxwell.

Received January 11, 1899.

ASPARTIC ACID METHOD.

1. The hypothetic principle of this method rests upon the assumption that the solvents used shall compare with the solvents that operate in the processes of soil disintegration, and plant-food preparation, in the field.[1]

2. The standards of control of this method are the ascertained results of the natural processes of soil decomposition in the field, under the conditions of climate and nature of the soils of the Hawaiian Islands, as indicated by the "results of cropping" and "the composition of the waters of discharge" flowing from the land into the sea.[2]

3. The sample is obtained by the mode given in previous publications; *viz.*, by the pipe, where this is practicable, otherwise by the spade. The calculation of available matter per acre is based upon the specific gravity (weight of the cubic foot) of the soil, and the depth to which the sample is taken. In thin soils the amount is less, in deep soils greater, than the amount found in one acre to a depth of one foot, upon which depth, calculations, so far, in the use of this method, have been based.

4. The solvent used in this method is aspartic acid. This acid was adopted because it was found that "aspartic acid dissolves phosphoric acid, lime, potash, and other bases (iron and alumina) out of the soil in almost the exact proportions that these ele-

[1] See the author's work on the "Lavas and Soils of the Hawaiian Islands;" also this Journal, 20, 107 (*1898*).

[2] See "Lavas and Soils of the Hawaiian Islands."

ments have been found in the 'waters of discharge,' and in which they are being removed by 'cropping.'"[1]

5. The method established and used so far, but which the author may modify in some features, is as follows: 200 grams of whole soil (not fine earth), air-dried, was put into a glass-stoppered Winchester quart bottle; to this soil was added 1,000 cc. of distilled water containing ten grams of pure aspartic acid, thus making a one per cent. solution. The bottle was gently shaken every fifteen minutes during the day portion of twenty-four hours (from eight o'clock A.M. to five o'clock P.M.). By "gently shaken" is meant that the bottle was taken up, and shaken in circular movement until the soil at the bottom was totally and thoroughly moved, but without ever rising above the surface of the solution, thus avoiding a remnant of the soil attaching to the sides of the bottle above the solution surface. This explanation is given because it has been shown that in "shaking the bottle containing the soil and solvent, which is the only mode of securing a uniform distribution and action of the solvent, the results of the action will be in large measure proportionate to the mode and vigor of the shaking."[2] At the end of twenty-four hours the contents of the bottle were emptied upon a filter, when 750 cc. of the clear filtrate were taken for analysis. The 750 cc. of filtrate was evaporated to dryness, and the residue gently ignited to remove all organic matter. The mineral residue was moistened with hydrochloric acid, evaporated and dried; then again softened with the same acid, warmed, and taken up with water, and filtered. After removal of iron and alumina from the filtrate with ammonium, the lime and potash were estimated in the usual way. The ammonia precipitate, containing also the iron and alumina, was dissolved in a little hydrochloric acid, neutralized with ammonia, the solution cleared with a little nitric acid, after which the phosphoric acid was precipitated and estimated by the common practice.

6. The estimation of the amounts of the elements that are "probably available for the immediate crop" is drawn from the foregoing analysis: As "a one per cent. solution of aspartic acid takes out of Hawaiian soils in twenty-four hours the same amounts of lime, potash, and phosphoric acid that are removed

[1] See "Lavas and Soils of the Hawaiian Islands," pp. 179–181.
[2] *Ibid*, pp. 136–138.

during the production of ten crops of cane, therefore one-tenth of these amounts may be taken as a nearest approach to the proportions of lime, potash, and phosphoric acid that are available for the immediate crop.''[1]

As it has been said, the principle of this method rests upon the assumption that the solvent used shall compare with the solvents that are actually operating in nature; and that the standards of control of the results of this method are the ascertained results of the natural processes of soil-decomposition in the field. Not any consideration has made it appear advisable to the author that a solvent should be used which is not found among the acids that result from vegetable existence and decay, and which consequently is not used by nature in the field. It has, on the other hand, appeared to him absolutely necessary that, before concluding that the results obtained by the use of any artificial method of examination are rational, and of any authority and value, these results should be subjected, if possible, to comparison with the standard of results actually following from the processes operating in the field.

HAWAIIAN EXPERIMENT STATION.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, NO. 5.]

TESTS FOR BORIC ACID.

BY VICTOR LENHER AND J. S. C. WELLS.

Received January 12, 1899.

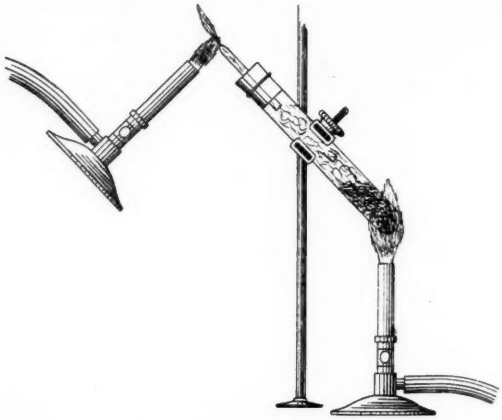
THE following investigation of the various tests for boric acid originated in an attempt to improve on the well-known boric ether or flame test.

In Newth's "Chemical Lecture Experiments," p. 227 (*1892*), is pictured and described an apparatus for producing this gas on a comparatively large scale. It occurred to us that this might be so modified as to make it useful as a qualitative test, and we devised the apparatus shown in the cut. It consists of a test-tube (six inches), fitted with a cork through which a glass-tube passes, the latter being drawn out so as to form a moderate-sized jet. In the test-tube is placed a mixture of the borate, concentrated sulphuric acid and alcohol, and the cork and jet

[1] See "Lavas and Soils of the Hawaiian Islands," p. 181.

tube inserted. The mixture is heated sufficiently in the Bunsen flame to freely volatilize the alcohol which then escapes through the jet and is burned in the flame of a second Bunsen burner. If boric acid is present, the flame will show its characteristic green tint.

In order to determine whether the test made in this manner was any more delicate than by the old method, solutions of known strength were made up, and comparative tests made of the two methods. In each of these tests, the following quantities of the different substances were taken: Borax solution, one cc.; sulphuric acid (sp. gr. 1.84), two cc.; and alcohol, ten cc. By the usual method, it was possible to detect the boric acid in



a solution, one cc. of which contained 0.01 gram of boron trioxide (B_2O_3). With the new apparatus we found that with a solution of one-tenth this strength (one cc. = 0.001 gram boron trioxide), a faint green color was perceptible, thus showing it to be an improvement on the test as usually conducted. Copper and barium salts were subjected to the same test, and it was found they did not interfere, giving no coloration to the flame.

These comparisons completed, we thought it advisable to carry our work still further and determine the degree of sensibility of the other tests in use. The fluoride test was made as follows: A bead of potassium fluoride and acid potassium sul-

phate was made in the loop of a platinum wire, at as low a heat as possible in order that the acid sulphate might not be decomposed. This bead was then dipped in the borax solution and heated in the Bunsen flame. A solution containing 0.01 gram boron trioxide in one cc. gave a faint green flame. With 0.001 gram per cc. no color was visible.

The glycerine test was also tried, the operation being conducted as follows: A bead of acid potassium sulphate was made and dipped into the borax solution, and then ignited sufficiently to decompose the sulphate and liberate the boric acid. After cooling, it was dipped into glycerine, and the latter ignited in the flame. On removing the bead from the flame, the glycerine continues to burn, giving a green flame if any boric acid is present. The limit of sensibility of this method was found to be a solution containing 0.001 gram boron trioxide per cc., this amount giving a faint green tinge to the flame.

Leaving the flame tests we now come to the one with turmeric paper. The solution to be tested was acidified with dilute hydrochloric acid, and the paper moistened with the acidified solution was dried at 100°. A solution containing only 0.0001 gram boron trioxide gave a distinct pink color on the paper, thus proving turmeric to be the most delicate of all.

In comparing the delicacy of the various tests, it is well to remember that the quantity of boric acid actually taking part in the bead and turmeric paper tests, is much less than the amount contained in one cc. of the solution tested. For example in the bead tests, one drop of the solution was sufficient to saturate the bead, and as one cc. was found to contain about fifteen drops the amount of boric acid actually used was only one-fifteenth of that present in one cc. For the tumeric paper test, two drops of the solution were ample.

In the following table the results have been calculated on this basis.

	Limit of test. Gram.	B_2O_3 actually present in test. Gram.	B_2O_3 in solution. Per cent.
Boric ether flame (old method)	0.01	0.01	1.0
Boric ether flame (new method)	0.001	0.001	0.1
Glycerine method	0.001	0.00006	0.1
Potassium fluoride and acid potassium sulphate method	0.01	0.0006	1.0
Turmeric paper method	0.0001	0.000013	0.01

Although the test with turmeric paper is by far the most delicate, it is a well-known fact that with the average student in qualitative analysis, the results are very uncertain; should a trifle too much acid be used to liberate the boric acid, the turmeric paper when dried will be brown instead of pink. If insufficient acid be added, there will be no boric acid coloration of the paper, even though considerable borate may be present.

The method that we recommend is intended to supplant the usual watch-glass or porcelain dish method that is in general use in most qualitative laboratories. Our modification of this method not only makes the test more delicate, but may be performed with the simplest apparatus; a test-tube, cork, and small piece of tubing are all that is necessary.

THE SPECIFIC GRAVITY OF CESIUM.

By A. E. Menke.

Received January 30, 1899.

THE specific gravity of cesium was determined many years ago by Setteler and given as 1.88. He, however, worked with relatively small quantities of the metal (0.6 and 1.1 gram) as his method of preparation did not allow him to obtain cesium in quantity. I have recently, in collaboration with Prof. Hugo Erdmann of Halle, made cesium on a large scale and it seemed to me advisable to redetermine the specific gravity.

The cesium for this purpose was purified by several redistillations in hydrogen, and then examined spectroscopically. The metal was weighed in hydrogen and then under liquid paraffin giving the following results as the specific gravity referred to water.

No. 1.	2.4001
No. 2.	2.4004
No. 3.	2.3996
No. 4.	2.4002
No. 5.	2.3998
No. 6.	2.4001
Mean	2.40003

In each case not less than four grams of metal were employed, and the proper correction made for hydrogen weighing.

These results change the atomic volume of cesium from the figure usually given (70.6 to 55.3) which does not make the drop

in the atomic volume curve from cesium to barium as abrupt as heretofore. It however affects the symmetry of the vertical column. The specific gravity of rubidium is probably not correct. I expect to redetermine it shortly.

The following parts of the atomic volume tables illustrate the points in question :

TABLE OF ATOMIC VOLUMES WITH SP. GR. OF CESIUM 1.88.

K..... 45.4	Ca..... 25.4	Sc..... 17
Rb 56.2	Sr..... 35	Y..... 24.8
Cs 70.6	Ba 36.5	La 22

TABLE OF ATOMIC VOLUMES WITH SP. GR. OF CESIUM 2.40003.

K..... 45.4	Ca..... 25.4	Sc..... 17
Rb 56.2	Sr..... 35	Y..... 24.8
Cs 55.3	Ba 36.5	La 22

These experiments confirm Beketoff's results on the atomic volume of cesium.

UNIVERSITY OF BERLIN.

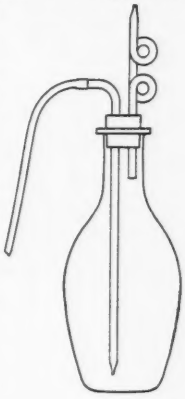
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LAFAYETTE COLLEGE.]

AN APPARATUS TO FACILITATE HYDROGEN SULPHIDE PRECIPITATIONS.

BY RICHARD K. MEADE.

Received January 21, 1899.

THE piece of apparatus described below has been in use here for the past term by the students of my class in qualitative analysis and answers fully the purpose for which it was designed : to hasten the precipitation of the copper-arsenic group by hydrogen sulphide. It consists of an ordinary flask or gas bottle of any suitable form and capacity, provided with a closely-fitting two-hole rubber stopper. A piece of glass tubing bent at right angles passes through one hole to the bottom of the flask, serving as an inlet for the gas. This is connected with the hydrogen sulphide generator by a half or three quarters of a yard of light rubber tubing. A piece of glass tubing bent in the gas flame to the form shown in the cut passes through the other hole and serves as an outlet for the gas.



The solution to be precipitated is poured into the flask, this in turn corked up, and the apparatus stood in the hood. The gas is now passed into the solution and the flask violently shaken by hand. The bends in the exit tube keep any of the solution from being thrown out of the flask. The churning up of the solution with the hydrogen sulphide gas quickly throws out of solutions the metals of the copper-arsenic group.

The young men tell me that not only is the time necessary for complete precipitation greatly shortened but the sulphides are obtained in a form more easily filtered and washed, by the use of this apparatus.

EASTON, PA., January 19, 1899.

ACTION OF A HARD WATER ON CERTAIN METALS.

BY JAS. LEWIS HOWE AND J. L. MORRISON.

Received February 25, 1899.

THE work described in this paper was undertaken for the purpose of studying the action of the town water supply of Lexington, Va., on brass, as complaint had been made by plumbers and others that brass faucets, valves, etc., were rapidly corroded by the water and rendered useless.

An analysis of the water furnished me by Col. N. B. Tucker, of the Virginia Military Institute, is as follows.

	Parts per 100,000.
Lime	7.30
Magnesia	4.065
Ferrous oxide	0.2057
Soda	0.3608
Carbon dioxide	30.196
Sulphur trioxide	0.2127
Silica	0.730
Chlorine	trace
Potash	absent

The relatively high proportion of magnesia is due to the fact that most of the limestone of the region is highly magnesian. Several different metals were tested and in each case a duplicate was made with distilled water. The method used was as follows: The metals were in thin strips except the brass which was in the form of wire. The surface was thoroughly cleaned with emery paper, the metal weighed, and the area of exposed

surface measured. With each metal two bottles of about a half-liter capacity and two open jars holding about two liters were used. One of the bottles was filled with town water and the other with distilled water and tightly corked, care being taken that no air should be in the bottle. One jar was filled with town water, the other with distilled water and left open to the air with a slight protection from dust. As the water evaporated more water was added. The temperature ranged from 10° to 20°, or occasionally perhaps 25°. After four months the metals were removed, and, after brushing off any loosely adhering deposit, weighed. The water was tested qualitatively for the presence of the metal in solution. The amounts of metal used in each case and the surface were approximately as follows: Brass, 36 grams, 105 sq. cm.; zinc, 56 grams, 170 sq. cm.; copper, 17 grams, 243 sq. cm.; iron, 64 grams, 391 sq. cm.; lead, 375 grams, 500 sq. cm.; aluminum (thin commercial sheet), 1.6 grams, 175 sq. cm.

In a further experiment a bundle of brass wire was packed in the pipes behind two of the laboratory faucets. One of these faucets (A) was used almost constantly all day, the other (B) perhaps half as much. These wires weighed respectively 36.540 and 36.527 grams and presented each 105.5 sq. cm. surface; these were left in position three and one-half months.

The results are expressed in the following table in terms of milligrams per square centimeter of surface:

BRASS.

	Loss or gain in weight.	
Town water, closed bottle,	0	Surface bright; no copper or zinc in water.
" " open jar,	0.047 loss	Surface bright, except at ends of wires; no copper but much zinc in water.
Distilled water, closed bottle,	0	Surface bright; no copper or zinc in water.
" " open jar,	0.019 gain	Surface bright except at ends of wires; no copper or zinc in water.
Faucet A,	3.742 loss	Surface showed much tarnish
" B,	1.108 "	Surface showed much tarnish

	Loss or gain in weight.	
ZINC.		
Town water, closed bottle,	1.54 gain	Surface slightly oxidized; zinc in water.
" " open jar,	2.523 "	Surface much oxidized; much zinc in water.
Distilled water, closed bottle,	0.348 "	Surface slightly oxidized; trace of zinc in water.
" " open jar,	0.1165 "	Surface slightly oxidized; trace of zinc in water.
COPPER.		
Town water, closed bottle,	0	Surface bright; slight trace of copper in water.
" " open jar,	0.16 loss	Surface tarnished, copper in water.
Distilled water, closed bottle,	0	Surface bright; trace of copper in water.
" " open jar,	0.131 gain	Surface tarnished, red to black; copper in water.
IRON.		
Town water, closed bottle,	0.025 loss	Surface slightly rusted; iron in water; 0.15 gram deposit.
" " open jar,	6.966 "	Much rust; iron in water; 4.575 gram deposit.
Distilled water, closed bottle,	0.077 "	Surface tarnished; iron in water; 0.085 gram deposit.
" " open jar,	7.086 "	Much rust; iron in water; 4.965 grams deposit.
LEAD.		
Town water, closed bottle,	1.304 loss	Surface bright; lead in water.
" " open jar,	1.152 "	Surface somewhat tarnished; little lead in water.
Distilled water, closed bottle,	2.306 "	Surface bright; lead in water.
" " open jar,	3.391 "	Surface much tarnished; much lead in water.
ALUMINUM.		
Town water, closed bottle,	0	Surface bright; no aluminum in water.
" " open jar,	0	Surface bright; no aluminum in water.
Distilled water, closed bottle,	0	Surface bright; no aluminum in water.
" " open jar,	0.128 loss	Surface much tarnished; aluminum in water.

This table reveals several points regarding the action on metals of a hard water containing an excess of carbon dioxide with considerable magnesia, and little sulphate and no chlorine.

1. Such a water acts readily upon zinc, far more readily than does distilled water, and it seems to be able to dissolve out the zinc in brass, leaving the brass much corroded. This would explain the action of the water on brass faucets, etc., above mentioned. Such a water should not be conveyed through zinc-lined iron pipes.

2. The hardness of such a water is no protection against its action on lead, this water having more than half as much action as distilled water when protected from the air.

3. Protected from the air, the action upon iron is comparatively slight.

4. Aluminum is perfectly resistant against a water of this character.

Similar experiments were carried out with nickel, but in no case did the water have any action upon it.

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NOTES ON THE ANALYSIS OF DYNAMITE AND GELATINE-DYNAMITE.

BY F. W. SMITH.

Received January 19, 1899.

I.

THE analysis of dynamite is not often described in text-books and the following notes, gleaned from some years' experience, may be of interest to those who have occasion to investigate such products.

A simple case is that of a dynamite containing nitroglycerine, sodium nitrate, wood-pulp, and basic magnesium carbonate or kieselguhr. The following process of analysis is recommended as giving satisfactory results. Weigh out ten grams on a pair of watch-glasses, place in a desiccator over sulphuric acid and leave for at least five days. The loss in weight is called moisture. Weigh about the same amount into a Gooch crucible and extract with pure ether. A drop of the ether is allowed to evaporate on a piece of tissue paper from time to time, and the extraction continued until the paper no longer tastes of nitroglycerine. Dry the residue in an air-bath at about 80° C. for two to three hours

and weigh. The loss minus the moisture is called nitroglycerine. In the case of powders containing only nitroglycerine and kieselguhr, this extraction is considerably more difficult, and it is advisable to remove the dynamite from the Gooch crucible to a small beaker and stir up with ether, washing the residue back when free from nitroglycerine. After extracting the nitroglycerine, the niter is extracted with cold water, and after the water ceases to extract anything it is displaced by acetone with the object of drying the residue without affecting the starch if any be present. The loss in weight is called sodium nitrate, potassium nitrate being very rarely used. The residue from the water extraction is ignited until free from carbon. The loss is wood-pulp, flour, bran, etc. I have found no satisfactory method for separating these, and rely on testing with iodine for the presence of starch as an indication of the presence of flour, etc.

If no earthy absorbents have been used, the ash after ignition is not likely to be over one-tenth per cent. of the whole sample. If the ash is considerable it is extracted with hydrochloric acid and the residue dried. The loss, expressed in percentages, is subtracted from the percentage of loss on ignition. The loss on ignition minus the loss on extraction with hydrochloric acid is called wood-pulp, etc., while twice the latter is entered as basic magnesium carbonate. This method saves a quantitative determination of the magnesia in the extract and rests on the fact that the basic magnesium carbonate employed as an absorbent loses practically one-half its weight on ignition. The extract should, however, be examined for lime, etc.; a small amount of iron may come from the kieselguhr. If any residue be left after extracting with hydrochloric acid it is examined under the microscope for kieselguhr, mica, etc., or it may be a small amount of venetian red used for coloring the powder.

The following analysis will serve to illustrate the methods:

No. 515.	Per cent.	Per cent.
Moisture	1.3	....
Nitroglycerine	39.6	39.6
Sodium nitrate	46.8	47.1
Wood-pulp	9.5	....
Basic magnesium carbonate	1.8	....
Kieselguhr	1.0	....
	100.0	

The loss on ignition was 10.40 per cent. and on extraction with hydrochloric acid 0.90 per cent. A quantitative determination of the magnesia, calculated as $Mg(OH)_2.3MgCO_3.3H_2O$, gave one and eight-tenths per cent. The portion used for moisture determination may be used to check the extractions.

Lunge's nitrometer may be used to advantage as a check on the analysis. About one-half gram of the dynamite is weighed into a small weighing bottle and about ten cc. of pure sulphuric acid poured over it. It is then allowed to stand from twelve to eighteen hours. In this time the whole usually goes into solution. In the cold the reaction is perfectly calm and no nitrogen is lost. It is then introduced into the nitrometer and decomposed as usual. The result is most conveniently expressed in cubic centimeters of nitric oxide per gram. On the sample mentioned above three determinations in the nitrometer gave: 237.0, 234.5, and 236.5 cc. of nitric oxide per gram. 39.6 per cent. of nitroglycerine gave 116.9 cc., 46.8 per cent. of sodium nitrate gave 122.9 cc. of nitric oxide per gram respectively, total 239.8 cc. The sodium nitrate used is generally ninety-six to ninety-eight per cent. pure; assuming ninety-seven per cent., reduces the calculated cubic centimeters to 236.1. The nitrometer work shows that in this case the ether-soluble portion contains nothing but nitroglycerine, the water-soluble portion nothing but sodium nitrate and its usual slight impurities. Eight minutes agitation in the nitrometer is sufficient for almost all cases.

II. GELATINE-DYNAMITE.

The gelatine-dynamites are considerably more difficult to analyze. The following analysis may be selected as typical:

No. 478.	Per cent.
Moisture	0.4
Nitroglycerine	33.7
Sulphur	1.9
Resin	7.0
Sodium nitrate	54.0
Guncotton	1.1
Wood-pulp	1.9
	100.0

The sample for moisture is weighed out as before. A filter cone (C. S. & S.) is dried and weighed in a weighing bottle and

about fifteen grams of the powder weighed into it. This is extracted in a Soxhlet apparatus with chloroform. The loss includes nitroglycerine, sulphur and resin. Sometimes the powder melts together in the hot chloroform, and in that case it must be taken from the filter and broken up in a beaker with cold chloroform until the bulk of the nitroglycerine is dissolved. After extracting with chloroform the residue is extracted with cold water to remove the sodium nitrate, dried and weighed, then extracted with acetone and the loss on extraction with acetone called guncotton. The still remaining portion consists of wood-pulp and earthy absorbents which are treated as above described. Sodium nitrate is appreciably soluble in acetone and should, on that account, be removed before the guncotton. It is often recommended to extract with acetone first and precipitate the guncotton with chloroform. This method gives results which are too high because the sodium nitrate dissolved by the acetone is also precipitated along with the guncotton. Allowance for this can, however, be made by incinerating the guncotton and calculating the ash as sodium nitrate. The second and following extractions can conveniently be made in the filter cone, setting it in a test-tube with perforated bottom. The filter is finally incinerated in a platinum dish with the residue, allowance being made for its ash content which in one case was 11.4 milligrams.

The chloroform solution is evaporated almost to complete absence of chloroform and taken up with glacial acetic acid. The precipitated sulphur is washed into a weighed Gooch crucible and washed further with a little strong alcohol to remove the resin. The nitroglycerine is determined by weighing a suitable portion of the powder (in this case one and two-tenths grams) into a small beaker. Ether is then poured on, and the powder worked over with a platinum spatula. The ether is several times renewed, being poured on a filter and collected in a glass evaporating dish. The ethereal solution is allowed to evaporate spontaneously in a cool place, the dish being covered with tissue paper. After twelve hours the residue can be washed into the nitrometer with acetic acid, care being taken not to use too much acetic acid which retards the reaction of decomposition, while if too little be used the reaction may be

extremely violent. Even with the greatest care in evaporation some nitroglycerine is lost and the results are usually about one per cent. low.

The calculated cubic centimeters of nitric oxide per gram on this analysis, assuming the guncotton to contain 11.9 per cent. of nitrogen, are 99.5 for the nitroglycerine, 141.7 for the sodium nitrate, and two and one-tenth for the guncotton; total 243.3. Two determinations in the nitrometer gave 243.8 and 242.7. As the sodium nitrate was certainly not pure, this result shows that the figure entered for nitroglycerine must be too low. Assuming the sodium nitrate to be ninety-eight per cent. pure gives 138.9 cc. and this, plus 2.10 cc. for the guncotton, subtracted from 243.2, total by analysis, gives 102.2 cc. for the nitroglycerine, corresponding to 34.6 per cent. Of course if necessary the water-soluble portion could be isolated and estimated in the nitrometer. The amount given in the analysis, 33.7 per cent., was determined by analyzing the ether-soluble portion in the nitrometer and calculating the nitric oxide obtained as $C_3H_5N_3O_9$. The resin in this case was recognized by its odor, and estimated by difference. An attempt to determine it in alcoholic solution, in presence of nitroglycerine, by titration with alcoholic potash, failed because nitroglycerine by itself is decomposed by alcoholic potash, decolorizing phenolphthalein solution. Some so-called flameless dynamites contain ammonium nitrate. The ammonia is estimated by distillation from aqueous solution and calculated as nitrate.

The two examples given cover the great bulk of dynamites and gelatine-dynamites used in the United States but many other mixtures, often of a very fanciful nature, are occasionally encountered, some of them exceedingly difficult if not impossible to analyze. The methods of analysis given in Guttmann's Manufacture of Explosives, Vol. II, are mainly reliable as far as they go, while some of Sanford's methods are likely to lead to disappointment. His separation of nitroglycerine from camphor is especially difficult to understand since nitroglycerine and carbon disulphide mix completely on the addition of camphor.

It is hoped that this paper will provoke discussion which may lead to the adoption of uniform methods of analysis by the chemists who have to deal with this class of products.

III. VARIOUS NOTES.

The nitrometer is conveniently set by the use of pure potassium nitrate. Exactly one-half gram is weighed into a weighing bottle, covered with sulphuric acid and allowed to stand until the solution becomes clear. The nitric oxide from this is brought into the measuring tube, and the amount of air in the reduction tube, which should also contain a few drops of water, is varied until the gas in the measuring tube shows 110.5 cc. with the air in the reduction tube at 100 cc. The use of potassium nitrate eliminates a large number of errors, such as those of reading the barometers, thermometers, etc. The potassium nitrate may be purified by dissolving it in the least possible quantity of cold water and precipitating with an equal volume of pure alcohol. Three times is generally sufficient, and the absence of chlorides and sulphates may be taken as a criterion of purity. Sodium nitrate, made by dissolving sodium in alcohol and neutralizing with dilute pure nitric acid, may be used as a check on the potassium nitrate. Leaky stop-cocks are a frequent source of annoyance in working with the nitrometer. The stop-cock of the measuring tube may be tested each time by allowing it to stay open for an instant after connecting it to the decomposing bulb by means of a thick-walled rubber tube and allowing the mercury reservoir to be at its lowest position. The mercury should not sink in the measuring tube. This assures the tightness of everything from the lower side of the stop-cock in the measuring tube to the upper side of the stop-cock in the decomposing bulb. The stop-cock in the decomposing bulb may be tested by analyzing the standard potassium nitrate, first with the level of the mercury in the reservoir about six inches above that in the decomposing bulb, and secondly about six inches below. If the first analysis shows too low a result, and the second too high, it points conclusively to a leak. A person having much nitrometer work to do must familiarize himself with the grinding of stop-cocks as they rarely leave the manufacturers' hands in a perfect condition. Grease for the stop-cocks is made from vaseline with the addition of Japan wax and rosin, the proportions being varied in summer and winter to get a product of suitable hardness and consistency.

The refraction method for the valuation of Chili niter gives results from one to one and one-half per cent. higher than those obtained by using the nitrometer and calculating the nitric oxide obtained as sodium nitrate. This is due to the almost unvarying presence of potassium nitrate, and the occasional presence of potassium perchlorate. The latter may be determined by fusing at a low temperature in the presence of powdered cupric oxide. The increase of chlorides after fusion is calculated as potassium perchlorate. The following is a complete analysis of one sample:

No. 471.	Per cent.
Moisture	2.2
Insoluble	0.1
Magnesium sulphate	0.2
Magnesium chloride	0.1
Sodium chloride	0.4
Potassium nitrate	3.6
Sodium nitrate	93.4
Potassium perchlorate	0.0
	100.0

The refraction method gave 96.8 per cent. of sodium nitrate by difference.

THE CALIFORNIA POWDER WORKS,
PINOLE, CONTRA COSTA COUNTY,
CALIFORNIA, January, 1899.

A MODIFICATION OF PIERCE'S METHOD FOR THE DETERMINATION OF ARSENIC IN ORES.

BY J. F. BENNETT, JR.

Received February 20, 1899.

THERE are several methods for the estimation of arsenic in ores in current use, many of which, however, are defective or do not approach the accuracy required even in technical work.

Pierce's method[1] (one of the best of those in general use), with or without Canby's modification, on account of its simplicity, is largely employed in metallurgical works notwithstanding the fact that it is subject to a range of inaccuracy which renders it inadmissible where accurate results are required, and which can be reduced to a minimum only by the most careful execution.

It is my purpose, after having pointed out the defective points

[1] Proceedings of the Colorado Scientific Society, Vol. I.

in the above method, to present what is thought to be an improvement upon it, intended especially for the determination of arsenic in ores, together with the results of a number of experiments carried on with a view to determining its accuracy.

Pierce, after getting the arsenic into solution as an alkaline arsenate, expels carbonic acid by boiling with an excess of nitric acid and then very carefully neutralizes with ammonia and nitric acid, using litmus paper as an indicator. By Canby's modification the neutralization is effected by means of an emulsion of zinc oxide.

As to the first method, I have found it practically impossible, after making a large number of determinations, to secure concordant results, especially on high grade ores. This is due to the fact that the silver arsenate is highly soluble in a slight excess of either acid or alkali, and slightly soluble in an aqueous solution of ammonium nitrate; while the precipitate under the conditions that exist here, even after vigorous stirring, invariably passes through the filter. I believe it is practically impossible to secure a neutral solution by means of the above reagents and indicator. Litmus paper, as is well known, is not a good indicator under the conditions as they exist above and I have found it entirely inadequate for the purpose of securing the degree of neutralization which is here absolutely indispensable.

Canby's method is little better in this respect, as the neutralization is only partly effected, the acid becoming too weak to attack the oxide but remaining sufficiently strong to dissolve the arsenate. The method which I propose for eliminating the defective points as above mentioned, is based on the following considerations:

(1). "The addition of sodium acetate to a mixed solution of arsenic and nitric acid is sufficient to insure the immediate precipitation of silver arsenate when silver ammonio-nitrate is introduced."[1] Also, silver arsenate is only "more freely soluble in acetic acid than in solution of ammonium nitrate."[2]

(2). The use of phenolphthalein as indicator instead of litmus paper.

(3). The precipitation, as herewith proposed, renders the precipitate granular and as easily filtered as silver chloride.

[1] Every, in Crooke's "Select Methods," page 420.
[2] Graham, in Storer's Dictionary of Chemical Solubilities.

Under consideration (1), the precipitation might be effected in a nitric acid solution, but in order to eliminate any solvent action which the presence of nitric acid might have, the precipitation is effected in a sodium acetate solution slightly acid with acetic acid, as will be seen in the scheme which follows: The absence of ammonia salts, etc., permits the use of phenolphthalein as indicator, thereby securing the neutralization promptly and without the tedious delay due to the slow action of the litmus paper. It will be noticed that I state above on the authority of Graham, that silver arsenate is somewhat more soluble in acetic acid than in ammonium nitrate, while I precipitate in acetic acid solution. I will say, however, that the above is a fairly strong solution of acetic acid, while my solution contains only a sufficient excess of acetic acid to destroy the color of the phenolphthalein (a drop or two of dilute acetic acid in 100 cc. of solution), in which I have found the silver arsenate to be practically insoluble.

The method is as follows:

One-half gram of the finely powdered ore is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate, preferably by mixing the ore with about two-thirds of the flux and using the balance as a cover. The mass is then heated gradually to complete fusion and kept so for a few minutes, cooled, and the soluble portion extracted with boiling hot water and filtered from the insoluble residue. The arsenic is in the filtrate as alkaline arsenate. Acidify filtrate strongly with acetic acid, cover and boil rapidly for a few minutes to expel carbonic acid; cool, add a few drops of a solution of phenolphthalein in alcohol, then a strong solution of sodium hydroxide to alkaline reaction; then one or two drops of acetic acid which will discharge the purple-red color if too much of the alkali has not been used. The solution should now consist of about 100 cc. Add, in slight excess, while violently agitating with a stirring rod, a neutral solution of silver nitrate, and allow to settle a few minutes, keeping out of direct sunlight. Pour the clear supernatant liquid through the filter, retaining the precipitate in the beaker, and wash once or twice by decantation with cold water. Finally throw the precipitate on the filter and wash

thoroughly with cold water. Now place the beaker in which the precipitation was made, under the funnel, fill the funnel full of water, and add twenty cc. strong nitric acid. When the filtrate has run through, wash filter thoroughly three or four times with cold water, make the filtrate up to about 100 cc., and titrate with a standard solution of potassium thiocyanate, according to Volhard;[1] or the silver may be determined by scorifying the filter and precipitate and cupelling. The former method must be adopted in the presence of chlorides.

Following are a few of a large number of determinations made to test the accuracy of this method:

Two hundred and fifty milligrams impure arsenic trisulphide (As_2S_3) were fused as above and the solution made up to 500 cc. Several portions of fifty cc., each containing 0.025 gram impure arsenic trisulphide, were taken and each portion treated as a separate determination from the point at which the filtrate is acidified strongly with acetic acid; then scorified and cupelled. Results are as follows:

TABLE 1.

No. of determination.	Weight of silver button. Gram.	Calculated amount of arsenic trisulphide found. Gram.
1	0.063915	0.02424
2	0.063240	0.02400
3	0.064720	0.02457
4	0.063450	0.02409
5	0.065075	0.02470
6	0.063675	0.02407

One-half gram impure arsenic trisulphide was fused and made up to 500 cc., and portions of 25 cc., containing 0.025 gram of arsenic trisulphide, were treated as above, except that the precipitate was dissolved in nitric acid and titrated with potassium thiocyanate (1 cc. = 0.02875 gram arsenic trisulphide) instead of scorifying and cupelling. Results are as follows:

TABLE 2.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic trisulphide found. Gram.
1	8.6	0.024725
2	8.6	0.024725
3	8.3	0.023863
4	8.6	0.024725
5	8.6	0.024725
6	8.7	0.025013

[1] *Ann Chem.* (Liebig), 190, 1.

It will be noticed that the first table gave uniformly low results. This was attributed to the loss of silver in scorification and cupellation, and in order to correct this loss four assays were run containing 0.06512 gram pure silver each, corresponding to 0.024725 gram arsenic trisulphide (the amount found by titration in numbers 1, 2, 4, and 5 in Table 2). The average loss was found to be 0.001 gram silver, which, added to the amounts in Table 1, gave an average result agreeing very closely with those of the above numbers in Table 2.

Following is Table 1 corrected for loss of silver in scorification and cupellation:

TABLE 3.

No. of determination.	Silver found as per Table 1. Gram.	Silver after correction. Gram.	Calculated amount of arsenic trisulphide. Gram.
1	0.063915	0.064915	0.024648
2	0.06324	0.06424	0.024392
3	0.06472	0.06572	0.024954
4	0.06345	0.06445	0.024472
5	0.065075	0.066075	0.025089
6	0.063675	0.064675	0.024457

Average amount of arsenic trisulphide 0.024670

One gram of leucopyrite was fused and made up to 500 cc. Portions of fifty cc. were treated as above and titrated with potassium thiocyanate (1 cc. = 0.0017536 gram arsenic). Results were as follows:

TABLE 4.

No. of determination.	Standard solution of potassium thiocyanate. cc.	Arsenic found. Gram.	Arsenic in ore. Per cent.
1	7.0	0.012275	12.275
2	7.0	0.012275	12.275
3	7.0	0.012275	12.275
4	7.0	0.012275	12.275

LABORATORY AGRICULTURAL COLLEGE OF NEW MEXICO, MESILLA PARK, N. M.

A SIMPLE VOLUMENOMETER.

BY C. E. LINEBARGER.

Received February 14, 1899.

McKENNA[1] has recently described a "New Apparatus for the Determination of Volume," which resembles in several respects one which I have devised and have been using

[1] This Journal, 21, 50 (*1899*).

for some time past. While in accuracy and ease of manipulation my apparatus possibly does not surpass McKenna's, it has the advantage of being readily constructed out of pieces of apparatus found in almost any laboratory, and also allows a very easy recovery of the solid whose volume has been determined.

A wide-mouthed bottle (two-ounce) is fitted with a twice-perforated rubber stopper or cork, if the liquid used attacks rubber. Through one of the holes is passed a ten cc. pipette, graduated in tenths of a cc. and permitting of the estimation of $\frac{1}{100}$ cc. Through the other hole passes a funnel tube with a short stem bearing a mark just below the widened part. The stem-end must be flush with the lower surface of the stopper so that the bottle may be completely filled with liquid without imprisoning any air-bubbles. A long piece of rubber tubing is attached to the upper end of the stem and provided with a good pinch-cock of any sort.

To use the apparatus, it is filled with liquid to a little above the stopper, great care being taken to remove all air bubbles. Suction is then applied to the extremity of the rubber tube so as to bring the level of the liquid in the funnel stem to the mark, when the cock is closed. The position of the liquid in the pipette is then noted, the hundredths of cubic centimeters being estimated. A weighed amount of the solid whose volume is to be determined is then placed in the funnel, and the liquid blown up and down gently until the solid is all washed into the bottle. The liquid is then brought to the mark on the funnel stem and the new position of the meniscus in the pipette read off. It is of course advisable to make several adjustments and readings of the levels and take their average.

To eliminate inaccuracy from change of the temperature of the liquid, the bottle may be packed in a box with some non-conducting material, as cotton-wool, etc. This seems to be a needless refinement, however, for the temperature of a laboratory changes but little during the time required for a determination, and it is not necessary to handle the bottle, so that it does not receive heat in that way. Moreover, the error is small compared with the error due to air adhering to the particles of the solid.

To show what results may be obtained with the apparatus,

full data are given for a series of determinations made with Ceylon graphite using kerosene as the liquid. The graphite was mostly in the form of a very fine powder, although many pieces as large as a grain of wheat were present. The kerosene had been dried by standing for three years over sodium shavings. The temperature of the liquid (about 20°) did not change by 0.5° during the experiments. Ten grams of the graphite were added each time.

READINGS ON PIPETTE.

Before solid was added. cc.	After solid was added.	After ten grams more solid was added.
9.92	5.67	1.42
9.90	5.67	1.44
9.91	5.64	1.43
9.91	5.66	1.43

Volume of ten grams of graphite..... $\begin{cases} 9.91-5.66=4.25 \\ 5.66-1.43=4.23 \end{cases}$

Density of graphite ..... $\begin{cases} \frac{10.00}{4.15}=2.35 \\ \frac{10.00}{4.23}=2.36 \end{cases}$

The apparatus was taken apart, cleaned, dried and reassembled, and two more determinations made. The volumes found were 4.22 and 4.26, respectively, and the corresponding densities 2.37 and 2.34.

Of course, other dimensions than those given above for the apparatus may be taken. Also, if it is desirable to know the temperature exactly, a thermometer may be introduced directly into the liquid by using a three-hole stopper.

THE SOLUBILITY, IN WATER, OF CERTAIN NATURAL SILICATES.

BY GEORGE STEIGER.

Received February 11, 1899.

IN this Journal for October, 1898, there is a preliminary paper upon this subject by Professor F. W. Clarke. The results shown in that paper were of such a character, that it was thought worth while to carry the investigation further, and an attempt has been made to show in what degree the different minerals are attacked by water after long standing.

The work was carried out as follows: One-half gram of each of the finely ground minerals was weighed out, and placed in a two ounce bottle with fifty cc. of water. These bottles were set aside where the temperature remained about 70° F. for one month, and were shaken from time to time. At the end of the period all were filtered, and the solutions were titrated with a standard hydrochloric acid solution, methyl-orange being used for an indicator.

What has gone into solution by this treatment I cannot say, sometimes soda, sometimes potash, possibly sometimes lime, but for the sake of comparison the results in the following table have been calculated in terms of Na_2O; although the percentage of sodium is very small in some of the specimens. I have given also in another column, the percentage of the combined alkalies as shown by analysis of specimens from the same localities.

	Formula.	Per cent. of combined alkalies by analysis.	Equivalent of Na_2O in solution.
Pectolite, Bergen Hill, N. J....	$Ca_2(SiO_3)_3NaH$	9.11	0.57
Muscovite.....	$Al_3(SiO_4)_3KH_2$	10.00	0.32
Natrolite, New Jersey.....	$Al_2(SiO_4)_3Na_2H_4$	15.79	0.30
Lintonite, Lake Superior.....	$Al_6(SiO_4)_6(CaNa_2)_3.7H_2O$	5.92	0.29
Phlogopite, Edwards, N. Y....	$Al(SiO_4)_3Mg_3KH_2$	9.32	0.22
Laumontite.....	$Al_2SiO_4Si_3O_8Ca.4H_2O$	1.00	0.18
Lepidolite, Maine.....	$\left\{\begin{matrix}KHLiAl_3(SiO_4)_3\\K_3Li_3(AlF_2)_3Al(Si_3O_8)_3\end{matrix}\right\}$	13.00	0.18
Elæolite, Litchfield, Maine....	$Al_3(SiO_4)_3Na_3$	21.17	0.16
Heulandite, Nova Scotia.....	$Al_6(Si_3O_8)_6(CaNa_2)_3.16H_2O$	2.00	0.13
Orthoclase	$KAlSi_3O_8$	16.00	0.11
Analcite.....	$NaAl(SiO_3)_2.H_2O$	14.00	0.10
Oligoclase, Bakersville, N. C ..	$\left\{\begin{matrix}AlNaSi_3O_8\\Al_2CaSi_2O_8\end{matrix}\right\}$	9.18	0.09
Albite.....	$AlNaSi_3O_8$	12.10	0.07
Wernerite, St Lawrence Co., N.Y	$\left\{\begin{matrix}Ca_4Al_6Si_6O_{25}\\Na_4Al_3Si_9O_{24}Cl\end{matrix}\right\}$	11.09	0.07
Leucite, Vesuvius, Italy.....	$KAl(SiO_3)_2$	21.39	0.06
Stilbite, Nova Scotia.....	$Al_2(Si_3O_8)_2(CaNa_2).6H_2O$	1.00	0.05
Chabazite, " "	$Al_2SiO_4Si_3O_8(CaNa_2).6H_2O$	7.10	0.05

It is worth noting in comparing the depth of color produced by phenolphthalein solution, as shown in Professor Clarke's

paper, with the percentage of alkali in solution as shown in this work, that some of the minerals which give a deep coloration with the former, show in the above table a comparatively small amount of alkali in solution, and *vice versa*. Muscovite for example while giving only a faint coloration with phenolphthalein, contained in solution alkaline compounds equivalent to 0.49 per cent. K_2O; pectolite, with 0.57 per cent. Na_2O, being the only one of the series showing a larger amount.

I hope in the near future to be able to carry this investigation further.

LABORATORY OF THE U. S. GEOL. SURVEY,
February 9, 1899.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY. NO. 6.]

A METHOD OF ANALYSIS FOR CANNED CONDENSED MILK.[1]

BY F. S. HYDE.

Received February 17, 1899.

BEFORE proceeding with the analysis, it may be desirable to ascertain the approximate specific gravity of the sample as follows:

Weigh the can with its contents. Then remove contents, replace with water to the top, and weigh again. Weigh empty can (sufficiently dried) and ascertain weights of milk and water separately. Divide the weight of condensed milk by the weight of water as a standard, and the quotient is the specific gravity of the condensed milk (near enough for practical purposes).

The specific gravity, which is not a matter of great importance, may vary from 1.27 to 1.37, according to the quantity of cane-sugar added, or according to the relative amounts of fat and albuminoid material in the milk used for condensation. That is, milk deficient in fat may show an increment in gravity irrespective of the amount of sugar added.

As to the method of analysis: the contents of the can, together with any portions of crystallized sugar, which may adhere to the bottom of the can like a hard mealy mass, are transferred to a beaker and stirred vigorously until the mass

[1] Read before the New York Section of the American Chemical Society, February 10, 1899.

becomes thinner and of the same consistency throughout. Then make stock solution as follows :

Stock Solution.—Weigh out twenty-five grams of the condensed milk and to this add seventy-five cc. water at ordinary temperature. This gives approximately 100 grams solution (of which twenty-five grams are condensed milk) of very nearly the consistency of cow's milk.

The writer attempted to simplify the method by taking aliquot parts of the stock solution for the various determinations, instead of weighing the different portions. Comparisons of the two methods gave discrepancies of three to five per cent. and the method of weighing was adopted as the more accurate, since an error of one-tenth cc. in measuring out five cc. for total solids may involve a difference of from one to two per cent. in the result. All results must be multiplied by four, since the condensed milk is diluted to one-fourth its strength ; *viz.*, each gram of solution should contain one-fourth gram of original condensed milk.

Total Solids.—Weigh out about five grams stock solution in previously weighed lead capsule (bottle cap two and one-half inches in diameter) or platinum dish. Evaporate on the water-bath to dryness. Finally heat in air-bath at 100° C. for fifteen minutes. Cool and weigh. Calculate the percentage and multiply by four.

Fat.—By Adams' coil, weigh quantity (five or six cc.) of stock solution in smallest beaker, recording weight of beaker and solution together. Without removing beaker from balance pan, insert the coil. When a sufficient quantity of solution has been absorbed, withdraw the coil, and reweigh the beaker with its residual contents. The difference is the weight of milk taken up by coil. Dry coil in air-bath at 100° from four to five hours, and extract with ether in the usual manner, employing a Soxhlet or Knöfler apparatus. Multiply the result by four.

Milk-sugar.—Dilute ten grams stock solution to 100 cc. Titrate direct with Fehling's copper solution. Calculate the percentage and multiply by four.

Cane-sugar.—Weigh ten grams stock solution in a No. 2 beaker. Add about fifty cc. water and five cc. (1 : 10) citric acid solution. Boil ten minutes. The citric acid inverts the cane-

sugar, but not the milk sugar. Condensed milk solutions do not coagulate readily with citric acid, hence filtration is superfluous. Cool the solution and neutralize with a solution of caustic potash, using litmus paper, and make up to 250 cc. Titrate direct with Fehling's solution in casserole over low flame. Make a duplicate titration to check results. Calculate reduction as due to cane-sugar, and then deduct milk sugar in terms of cane. The Fehling's copper solution should contain 69.28 grams copper sulphate per liter (five cc. equal to 0.05 gram glucose). On mixing equal volumes of the copper and alkaline tartrate solutions:

Ten cc. should equal 0.0500 gram glucose.

Ten cc. should equal 0.0678 gram milk sugar.

Ten cc. should equal 0.0475 gram cane-sugar (by inversion).

Example:

Suppose 10.16 grams stock solution are taken, inverted, and made up to 250 cc. as above; and suppose, on titration, nine cc. of this diluted solution is found equivalent to 0.0475 gram cane-sugar. Then 250 cc. should contain 1.3194 grams cane-sugar, or 12.98 per cent. (if all sugar in 10.16 grams stock solution be calculated as cane). Since the stock solution is one-fourth the strength of the original condensed milk by dilution, then 12.98 per cent. cane-sugar multiplied by four equals 51.92 per cent. cane-sugar. Now deduct the per cent. of milk sugar in terms of cane-sugar. Assume that milk sugar has been found to be 12.796 per cent., which is equivalent to 8.96 per cent. cane-sugar; then 51.92 per cent. minus 8.96 per cent. equals 42.96 per cent. cane-sugar as such.

It will be observed that while the method of calculation is not new, yet the results obtained are dependent on the manner of making up the milk solution, and weighing the quantities taken for analysis, instead of taking aliquot portions, as in the old methods.

Casein, Albumen and Salts.—The difference between milk solids, and the sum of the milk sugar and fat, is casein, albumen, and salts. For proteids alone, make a nitrogen determination by the Kjeldahl method.

Water.—The difference between 100 per cent. and the per cent. of total solids gives per cent. of water.

Milk Solids.—Subtract cane-sugar from total solids.

Ash.—The content of ash varies with amounts of cane-sugar present. It may be determined by igniting total solids in a platinum dish.

Degree of Condensation.—This depends on the extent of condensation at factory, as well as the amount of total solids in the original cow's milk used. It is rather an uncertain figure, since skimmed milk might be used. Calculation is usually made by dividing the percentage of milk solids in the condensed milk by 12.5 per cent., the average for ordinary cow's milk. Some recommend calculation based on the percentage of 'solids not fat.'[1]

In regard to the determination of cane and milk sugars in condensed milk with Fehling's solution, when the milk solutions are sufficiently dilute, the end-reaction may be easily determined without the use of the ferrocyanide indicator and the consequent loss of time in preparing ferrocyanide solutions and making filtrations will be avoided.

The condensed milk solution is titrated directly, without coagulation and filtration, in a four-inch casserole over a low Bunsen flame. When the titration is nearly completed it will be noticed that the red precipitate of cuprous oxide and organic matter seems to suddenly collect and settle, on removal of the heat, leaving a clear supernatant liquid which may be either bluish or yellowish, according as the titration is "under" or "overrun." This is all the more apparent in a casserole.

If the supernatant liquid is still slightly bluish, when tilted against the white sides of the casserole, a few drops more of the milk solution will discharge the color, such decolorization being the end-reaction. This end-reaction has been carefully compared with the ferrocyanide indicator, and the difference is too small to be of practical importance, when rapidity is an essential feature of the analysis.

With very little practice, the eye becomes accustomed to the change (discharge of color) and the value of the method can best be appreciated when it is necessary to execute several analyses in a short space of time.

Citric acid employed for the inversion of the cane-sugar, not-

[1] See McGill: *Analyst*, May, 1898, p. 128.

withstanding statements of various authors to the contrary, usually does not produce coagulation in condensed milk solutions, even on boiling. Unless necessary to resort to prolonged operations for coagulation and filtration with special reagents, it is advisable to make use of dilute solutions directly, and avoid any errors in coagulation and filtration, which might not compensate for discrepancies in titration.

It is generally admitted that the presence of organic matter, other than sugar, exerts a reducing action on Fehling's solution while at the same time concentration by evaporation and rapidity of titration also influence the results, so that, whether coagulation and filtration are employed or not, the final results cannot be considered as absolute.

The amount of cane-sugar averages between thirty and forty per cent., and the fat below twelve per cent., which is not surprising in a manufactured article. In the so-called evaporated milks or creams, the cane-sugar is usually absent. The presence of cane-sugar seems to be essential as a preservative and to make the canned condensed milk palatable. Polarimetric methods may be employed for estimating the sugars, but extra reagents are required for clarifying the solutions, besides a correction for the volume of precipitated solids.[1] The old Fehling method is quicker and the results quite satisfactory. Again, it is claimed that the heating during the process of manufacture of condensed milk alters the rotatory power of the milk sugar, while its power to reduce alkaline copper solutions is not seriously affected.

In the Report of the Brooklyn Health Department for *1895*, p. 270, will be found a list of condensed milk analyses, which, with two or three exceptions, were performed by the writer according to the method submitted. The results are hereby appended for ready reference :

[1] See Leffmann and Beam's Analysis of Milk and Milk Products, (*1896*), pp. 70–73.

CONDENSED MILKS ANALYZED DURING 1895.

Brand.	Total solids.	Milk solids.	Milk sugar.	Cane-sugar.	Fat.	Casein, albumen, salts, etc., by difference.	Water.
A.....	77.56	40.78	14.04	36.78	9.53	17.21	22.44
B.....	78.04	44.22	10.14	33.82	10.56	23.51	21.96
C.....	75.12	41.96	15.71	33.16	8.92	17.33	24.88
D.....	75.32	37.36	12.28	37.96	9.04	16.04	24.68
E.....	76.72	36.72	9.50	38.00	8.84	20.38	23.28
F.....	78.82	44.92	10.64	33.90	10.35	23.93	21.18
G.....	74.72	41.71	13.12	33.01	7.84	20.75	25.28
H.....	77.12	42.28	12.80	34.84	9.80	19.68	22.88
I	77.72	45.81	11.96	31.91	9.52	24.33	22.88
J	71.16	38.25	12.52	32.91	9.04	16.69	28.84
K.....	76.40	39.91	11.92	36.49	8.68	19.31	23.60
L	79.12	47.29	11.06	31.83	10.38	25.85	20.88
M	75.64	42.73	17.20	32.91	9.18	16.37	24.36
N.....	74.96	40.37	12.24	34.59	9.92	18.21	25.04
O.....	77.56	43.21	10.76	34.35	8.40	24.05	22.44
P.....	77.72	45.91	12.56	31.81	8.56	24.79	22.28
Q.....	75.76	46.82	10.84	28.94	10.03	25.95	24.24
R.....	73.72	30.76	12.79	42.96	8.07	9.89	26.28
S.....	35.24	35.24	12.32	none	11.82	11.10	64.76
T.....	34.33	34.33	11.27	none	9.76	13.30	65.67
U.....	30.46	30.46	10.15	none	6.73	13.58	69.54

The last three analyses represent so-called "Evaporated Milks," containing no cane-sugar.

A law of New York State,[1] requires that no "condensed milk shall be made * * * * unless the proportion of milk solids shall be, in quantity, the equivalent of twelve per centum of milk solids in crude milk, and of which solids twenty-five per centum shall be fats."

Generally, the amount of fat in condensed milk is less than ten per cent. of the whole, or less than twenty-five per cent. of the forty per cent. (more or less) milk solids of which the fat is a part.

The original cow's milk used may be considerably above legal standard, and yet the degree of condensation be insufficient to bring the manufactured article within the requirements of the law. Under such conditions, the manufacturer might be liable to prosecution, although the product might be perfectly wholesome.

As to preservatives, the manufacturers seem to depend almost entirely on the use of cane-sugar in sufficient quantity.

[1] Sec. 25, Chap. 143, L., 1894.

REVIEWS.

ON RECENT PROGRESS IN PHOTOCHEMISTRY.[1]

The term "photochemistry," as we intend to treat it, is to be taken in a broader sense than that which is usually accorded to it. It is proposed to express by it more than the influence which light exerts in stimulating chemical activity. The chemical manipulations, reactions, and general manifestations are all instrumental in bringing about the visible effects of this action and should not be isolated from it in treating the subject.

Let us confess at the outset that the influence which light exerts upon silver haloids is still enigmatical. We cannot even to-day say positively what occurs in this case, chemically speaking. It cannot be said without decisive proof that a subhaloid or a perhaloid has been produced, nor can we prove that silver has been reduced to the metallic state.

We may perhaps be permitted to suppose a transformation of the vibrations which we call light into those which may be called chemical vibrations.

When light vibrations impinge upon a mixture of hydrogen and chlorine, it is surely not merely havoc which results, but a rythmic system is produced. With bromine and hydrogen this action takes place in a similar manner, but at higher temperatures. Heat vibrations as well as light vibrations are here perhaps transformed into chemical vibrations.

It requires great strength of scientific faith to believe that in all these actions the light vibrations play merely the part of that famous tip of an eagle's wing, which, accidentally disturbing the repose of a snowflake, causes the avalanche to proceed upon its destructive path downward into the valley.

That light vibrations on impinging upon a chemical compound, such as silver bromide, turn latent within this compound without really decomposing it, has long since been virtually shown by the fact that those parts of a photographic dry plate, thus affected, really exhibit this condition by the readiness with which they are attacked by reducing agencies, suitably applied. This manner of looking at the developing of a photographic negative has never as yet been attempted, or if so, not to our knowledge.

This conception is in no way rendered invalid by the recent observation of T. Sterry, that an exposed but not developed dry plate may be freed from unchanged bromides by immersion into

[1] Read before the New York Section of the American Chemical Society, December 9, 1898.

sodium hyposulphite solution, and after this has been done it may be developed in gaslight by a developer containing silver nitrate. Sterry assumes that in reality two latent pictures exist within the exposed film, the first of which he calls the inorganic, the second, just mentioned, the organic one. If our own conception is upheld this differentiation would be needless, because the hyposulphite solution does not dissolve the parts of bromide that had been altered, perhaps by reason of changed stress within the molecule.

The following facts pointing in the direction of the views above stated may be cited :

Attention in the first place is called to the well-known appearances concerning phosphorescence paint. It is impossible to believe that the light vibrations are merely "bottled up" within the luminous paint, for the light given off is never of the same quality as the light received.

A very simple experiment shows this: A glass plate, upon which a smaller ruby glass plate is allowed to rest, is coated with luminous paint and exposed to sunlight. After some time the plates are taken into a semi-dark room, and we observe, on removal of the ruby glass, that the part which has been covered appears bright lemon-yellow, while the rest of the plate shines with its peculiar lavender-colored hue.

The red waves have in this instance been changed into yellow ones. Or, if the ruby glass should have allowed yellow waves to pass through (which, however, is not likely) we must conclude that the red waves had been absorbed.

If we use for the purpose of expressing the difference of color between the light received and that emitted the terms, borrowed from electric terminology,[1] "step-up," and "step-down," we have in our experiment, just described, to do with a "step-up." With blue glass, under similar conditions, we obtain a more reddish yellow, a "step-down."

In order to show how the vibrations communicated in some way to the phosphorescent plates may be made to further exert their activity, I shall now refer to the experiments of Prof. Zenger, director of the observatory at Prague. Zenger exposed a phosphorescent plate in a camera, provided with a prism, to the solar spectrum. He obtained a picture of the same in its entire length, from ultra-red to ultra-violet. We may remark incidentally that Fraunhofer's lines appear on the phosphorescent plate as bright lines in the red and as dark lines in the violet part of the spectrum. Zenger proceeded then to face the phosphorescent plate in a printing frame, in the dark room, to a sensitive dry-plate. Later on he developed the dry plate and thus obtained a permanent picture of the spectrum.

[1] See W. Goold Levison: On a system of classification of luminescent substances, New York Academy of Sciences, December 5, 1898.

In speaking about phosphorescence we must not forget to call attention to the recent research of Wiedemann and his co-workers. The facts most interesting to us about these observations are those of transformation of radiant energy into chemical energy and vice versa of chemical into radiant energy. Wiedemann introduced a new terminology for the generic word phosphorescence. He calls all the pertaining phenomena collectively "luminescence," of which phosphorescence is only a special case.

We may call the fact of a body becoming luminous 'normal' if primarily the oscillations caused by the agency of heat are increased to such a degree, that different oscillations, which we recognize as light, are produced. But besides this kind of generation of light we know another one in which external causes, without corresponding increase of temperature, produce light. This second kind of exciting light Wiedemann calls luminescence.

Photoluminescence is then produced by light as an impinging cause. This, according to its persistence or to its instantaneous appearance, has to be termed phosphorescence or fluorescence. Electric discharges, causing light appearances in gaseous bodies, produce electroluminescence. We notice that Wiedemann found that even here the temperature lies frequently far below the temperature sufficient to cause the incandescence of such gases.

Light caused by certain chemical processes is called "chemiluminescence;" that produced by gentle warming, *e. g.*, of fluorspar "thermoluminescence." Light appearances caused by friction are called "triboluminescence;" by crystallization are called "crystalloluminescence;" and by solution, "lyoluminescence."

Without attempting to enter in detail upon this new and interesting field of study we allow our attention to be drawn to some experiments of chemical interest. Lenard and Wolf found that if a photographic negative, newly developed by means of (potash) alkaline pyrogallol and sodium sulphite, is slightly washed and then put into the alum-bath, in the dark, that in the first instance the plate and subsequently the entire bath appear highly luminous. They observed the phenomenon in developing a stellar photograph and sought for the cause. Chandler supposed the sensitive film to be the cause. Phosphorescence, induced by alumina precipitated by potash, was excluded. A true chemiluminescence was found to obtain. This luminescence, however, did not take place if alumina was not precipitated. We know that an excess of potash as well as of alum may prevent such precipitation. On the other hand, precipitation was not always accompanied by luminescence. If sodium sulphite or

pyrogallol were left out of the solution, the most perfect precipitation without luminescence occurred.

In short, though the proportions of the developer were changed in many ways it was not only shown that sulphite must not be present in excess nor in too small quantities (above 1.25 per cent. or below 0.13 per cent.), in order to produce the effect; in the same way an excess of pyrogallol above 0.3 prevented it, but 0.005 per cent. pyrogallol sufficed to produce it. Evidently, in order to successfully perform the experiment, a fifth substance, not intentionally introduced into the developer, was at work right along. Observation showed that the precipitated aluminum hydroxide after luminescence had occurred, had carried down all the pyrogallol, the supernatant liquid was colorless, the precipitate yellow. Suspicion was aroused that alumina, in its finely divided condition, had fixed upon its surface not only all of the pyrogallol but also oxygen, which was proved to be the sought-for fifth substance. The luminescence was the consequence of a sudden energetic oxidation of pyrogallol.

The proof was rendered in many ways. The experiment was performed in presence and in absence of air. In the first case luminescence occurred, in the latter not. A further experiment was performed in presence of oxygen, when luminescence appeared brighter than ever.

A conundrum, however, was offered in the fact that sodium sulphite, an oxygen consumer, purposely added to developers to prevent spontaneous oxidation of pyrogallol (*e. g.*) was nevertheless necessary to bring about the phenomenon.

The curious fact was experimentally established that the pyro-sodium sulphite potash developer used up oxygen less swiftly than did pyropotash alone, thus the developer containing sulphite remains richer in free oxygen than without it.

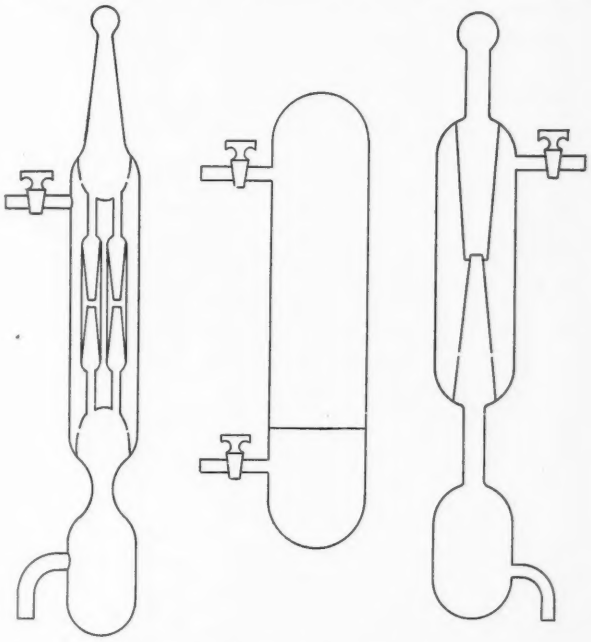
This is one example of true chemiluminescence caused by oxidation of pyrogallol.

Another, still more interesting, example of chemiluminescence is offered by the appearance of what was formerly called "sea-phosphorescence." This luminous appearance of the ocean, according to newer researches of Otto, is the consequence of oxidation of organic matter by means of ozone. Water, introduced together with ozone into the apparatus shown in the accompanying figures, will turn highly luminous upon agitation. Distilled water will not show the effect, but upon addition of urine, alcohol, benzene, or other suitable oxidizable material, luminosity will appear.

It may be of use to those present interested in photography, to say a few words about the changes in developers. There is in the first place a developer to be mentioned, producing color tones in dia-positives for the purpose of projections. We all

know how important a factor is the suitable color for a given picture.

Silver chloride gelatine plates should be used (similar to the mixture on the Aristo papers) and the plates are not printed out under the negative. The outlines of the picture must faintly



show in daylight, to which they should be exposed for one to three minutes, according to the kind of light and of the negative. As a uniform developer, paramidophenol is recommended by Hanneke, of the Berlin-Charlottenburg photochemical laboratory.

Distilled water	1000 cc.
Crystallized sodium sulphite	50 grams
Citric acid	8 "
Paramidophenol hydrochloride.....	7 "

In this manner pictures in yellowish-brown tints are obtained; carmoisin, violet to steel blue tints, are produced subsequently in a gold-bath containing ammonium thiocyanate. Acetone and aldehyde are beginning to take the place of alkalies in our

developers. The brothers Lumière and Seyewetz were the first to recommend these substances.

Water	500 cc.
Sodium sulphite (double usual amount to produce black tone)	200 grams
Concentrated sulphuric acid	10 drops
Pyrogallol	14 grams

Fifteen cc. of this and five cc. acetone and dilution to 50–120 cc. with water. Excess of acetone produces a greenish color. Acetone is said to harden the film. Consequently this developer is of importance for photographic work in tropical climates. It is not necessary to use C. P. acetone but the commercial product of boiling-point +56°–58° C., which costs about thirty cents per pound, suffices.

Bromide paper developed with acetone developer will be found free from blisters. The aldehyde developers, in contrast to the acetone developers, are rapid workers and they require an ample addition of potassium bromide.

Water	100 cc.
Sodium sulphite	15 grams
Formaline (forty per cent.)	2 cc.
Hydroquinone	1.5 grams

Ordinary ethyl aldehyde (fifty per cent.) can be used also, while benzaldehyde, acetophenone, and benzophenone, which can only be used in alcoholic solution, are practically useless. Dr. Andresen furnishes a list of reactions of the current developers. He includes in his list the following:

Amidol = Hydrochloride of 2,4-diamidophenol.
Eikonogen = α-Amido-β-naphthol-β-sulphonic acid.
Glycin = p-Oxyphenylglycin.
Hydroquinone.
Metol = Methyl-p-amidophenyl sulphate.
Ortol = Methyl-o-amidophenol sulphate, mixed with hydroquinone.
Paramidophenol hydrochloride.
Pyrogallol.

In regard to the use of formalin for photographic purposes it is a fact worth recording, that the expansion of paper, consequently any distortion whatever of the picture, may be avoided by previous immersion of the paper in a two per cent. formalin solution and subsequent drying.

The sensational news, which passed some time ago through our daily papers, embellished by appropriate pictures, suggestive of spiritistic productions, were based upon the observation of Dujardin, that imprints of the human hand may be produced

within the developing bath upon dry plates. It was found that the animal heat produced these pictures and that a direct contact of the plate with the hand, only shielded by another glass plate, is necessary. If the covering glass plate was separated from the dry plate (both in the developer) by means of glass rods or glass cubes, no action occurred.

It is gratifying to the chemist to observe how chemistry enters in almost every direction as a handmaid into practical photochemical pursuits.

Lieutenant Kiesling has constructed a magnesium light apparatus, avoiding the smoke attending the use of this element. He allows salt-mouthed vials of 250-400 cc. capacity filled with dry oxygen (directly from the gasometer), and containing magnesium ribbon and a fuse, or an electric wire system, to oscillate like a pendulum. The bottom of the little vials is covered with a small quantity of plaster of Paris or asbestos. It is said of magnesium burnt in oxygen that it furnishes a light the actinic action of which is twelve times as great as if burned in air. The little vials remain useful for twenty-four hours. Acetylene light has also been recommended.

Dr. Roberts, Director of the Archæological Museum in Halle, observed that in a collection of silver coins of the fifth century B. C. (Tetradrachms) had suffered a change on the surface of the side exposed to light. The analysis of the thus changed surface proved this to consist of silver chloride. An attempt is made to explain this by showing that these coins had for centuries been resting in sand containing NaCl. A coinage from silver containing silver chloride is excluded since the interior parts of the coins were proven to consist of tolerably pure silver.

A comparatively new field of research is opened up by the study of what makes an organic substance a developer. What are the groups with developing functions? A. and L. Lumière and Seyewetz have studied the influence in this direction of alkyl-substitutions in groups possessing developing functions.

As a general rule it has been granted that the faculty of developing the so-called latent picture, exists in compounds containing at least two hydroxyl groups in ortho or para position.

These authors have studied the para-compounds of amidophenols and of polyamines for which the above rule was still under discussion.

Paraphenylendiamine and paramidophenol were subjected to alkylization, and the following substitution-products were prepared and tested in regard to their developing properties:

1. Monomethylparaphenylenediamine, $C_6H_4\begin{cases}NH.CH_3 & (1)\\ NH_2 & (4)\end{cases}$

2. Dimethylparaphenylenediamine, $C_6H_4\begin{cases}N(CH_3)_2 & (1)\\ NH_2 & (4)\end{cases}$

3. Tetramethylparaphenylenediamine, $C_6H_4\begin{cases}N(CH_3)_2 & (1)\\ N(CH_3)_2 & (4)\end{cases}$

4. Monomethylparamidophenol, $C_6H_4\begin{cases}OH & (1)\\ NH.CH_3 & (4)\end{cases}$

5. Dimethylparamidophenol, $C_6H_4\begin{cases}OH & (1)\\ N(CH_3)_2 & (4)\end{cases}$

6. Paranisidine, $C_6H_4\begin{cases}O.CH_3 & (1)\\ NH_2 & (4)\end{cases}$

The compounds 1 to 5 are developers. 1 to 3 may even be used as such without the addition of alkali. 6 was without developing power.

The alkylization, as far as shown, therefore, does not destroy the developing power. We must remember that the alkyl-substitutions into an amido group weaken its basic properties but do not entirely destroy them. On the other hand, if a hydroxyl of a phenol suffers alkylization the phenol properties are lost entirely (as in 6), as are the acid properties in most neutral salts, and the developing power is correspondingly lost.

Leaving the chapter of the chemistry of developers we record a number of various items of general interest.

Glycerol has been successfully used instead of alum in electric light projection. The lenses as well as the diapositives are endangered by the high temperature of the arc light. For the celluloid films of the kinematograph this danger is obvious. The alum cell heretofore used is sometimes brought up to boiling and in the best case it will form bubbles. Glycerol has been used even between the source of light and the condensing lens. After a performance of two hours under these conditions with an electric lamp of 2000 candle-power, the glycerol (which does not form bubbles and boils at $+290°$ C.) registered $+80°$ C. Pure glycerol being practically colorless, the light is not in any way weakened.

Talking about the kinematograph, it may be worth while reminding this audience of the immense proportions which the applications of photochemistry have assumed in this country. Mr. Dunn ordered from the Eastman Co. three kinematograph films, each 50,000 feet long. Each film was said to cost $10,000. The films were intended to be used at the occasion of the Corbett-McCoy contest in Buffalo, and three apparatus to work

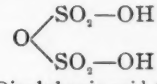
simultaneously in order to secure at least one good copy. Each film of 50,000 feet was supposed to run for eighty minutes (625 feet per minute) and twenty-seven pictures were to be taken per second.

The use of the most varying chemicals for photochemical pursuits is surely on the increase and it happens frequently, as we stated at the outset, that the chemist is confronted with reactions quite difficult to understand.

A case of this kind is offered in the use of ammonium persulphate for the purpose of softening hard negatives. This technical term means, in common language, that a negative which shows too strong contrast between high lights and shadows has to be brought down to more uniform delineation by chemical action. Mechanical rubbing down of the denser parts by means of alcohol, or local or entire reduction (as it is styled) by means of potassium ferricyanide and sodium thiosulphate, were tedious and sometimes doubtful modes of procedure.

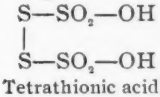
The ammonium persulphate in a five per cent. aqueous solution has the faculty of attacking the denser parts, without injuring the detail in the shadows of the negative. Ammonium persulphate is a salt of persulphuric acid. We are in this instance agreeably reminded of Kekulé's lucid way of showing at a glance the similarities in the constitution of compounds.

Water.



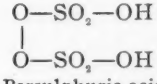
Disulphuric acid (or pyrosulphuric acid).

Hydrogen persulphide.



Tetrathionic acid.

Hydrogen peroxide.



Persulphuric acid.

The acid itself has not been prepared, but its salts are in use as oxidizers. They are mostly prepared from ammonium persulphate, which is obtained by electrolysis of ammonium sulphate.

The action of ammonium persulphate upon a negative is still under discussion. While some claim that a soluble double salt, $NH_4O.SO_2.OAg$, is formed, others assert that ozone is generated, as with hydrogen peroxide.

There is a chance for still further study. We cannot conclude this brief summary without referring to the action of most varying substances upon dry plates. Not only do certain vapors, but also matter from which no material vaporization can otherwise be noticed, attack the sensitive film of a photographic plate.

Messrs. Muraoka and Kasuya, in Kyoto, Japan, made a study of the light of glow worms. In addition, they experimented in the direction just now referred to. I quote their own words: "We also experimented with magnesium oxide and cadmium oxide. The first has no action, but the latter shows a curious behavior, inexplainable either by radiation or vaporization. We took two thick pieces of card-board, A and B, both of the size of a photographic dry-plate; from the center of A we cut out a small square and from that of B a large square. A was put upon a glass plate and the square cut away was filled with powdered cadmium oxide. Then A was covered with B and the dry-plate was put on top of B. We expected to find that the plate would be attacked all over the area of the larger square of B, since the vapor from the smaller opening could have easily spread to the edges of the larger square. But on developing the plate it was found that the blackening was restricted to the size of the smaller square.

If A is separated from B to the distance of 1 cm. and a copper wire is stretched between the two without touching them, no blackening will be produced above the copper wire. According to this, a radiation appears to be at work, but it remains inexplainable why this radiation does not also obliquely extend to the larger square."

It may interest you to hear of experiments performed by myself with the view of practical application. I faced daguerreotypes to dry-plates in a printing frame and obtained faint but very clearly outlined copies. These copies became more distinct, very likely by contrast, when I exposed the frame to light, the dry-plate being thus blackened to the extent of about two inches all around the impression made by the daguerreotype.

References: Photographische Mitteilungen, January, 1898, to November, 1898.

Annalen der Physik und Chemie, **64**, No. 1 (*1898*); **34**, No. 7, (*1888*); **34**, No. 8*b* (*1888*).

COLLEGE OF THE CITY OF NEW YORK,
December, 1898.

L. H. FRIEDBURG.

A REVIEW OF THE PRESENT KNOWLEDGE OF SODIUM NITRATE, TOGETHER WITH THE ORIGIN, PRODUCTION, AND DESTRUCTION OF NITRATES IN THE SOIL.[1]

The importance of nitrates in technical processes, as well as in providing a quickly and certainly available plant food for admixture with chemical fertilizers, or for use alone, by the agriculturist, cannot well be overestimated. It is comparatively a few years since the vast stores of sodium nitrate in Chili have been sufficiently exploited to impress the world with their importance as a source of supply for the above demands, and I apprehend that the president of this society felt that it would not be time wasted when he invited me to direct the attention of the society to the origin, and to some of the uses of sodium nitrate, and also to some of the recent extensions of scientific knowledge in regard to the production of nitrate within the soil.

The rate at which the use of sodium nitrate is increasing in the United States, is shown by the following:

In 1897 the deliveries for January alone were 60,000 bags.
In 1898 " " " " " " 80,000 "
In 1899 " " " " " " 90,000 "

The yearly consumption in the United States for 1897, was 700,000 bags; for 1898, 975,000 bags. The total consumption of the world for 1897, was 8,050,000 bags; for 1898, 9,235,000 bags. A bag is approximately 300 pounds. The increased consumption in this country during the past year was 275,000 bags. These figures refer only to the Atlantic ports.

It speaks volumes for the influence of scientific men upon the development of practical agriculture in the world, when we remember that it is scarcely ten years since the agricultural experiment stations and scientific investigators began to vigorously direct public attention to this source of plant food. In fact, in this country, it has scarcely been so long, and it is only within the last two or three years that our experiment stations have been able to readily procure it.

There are two reasons for this rapid development:

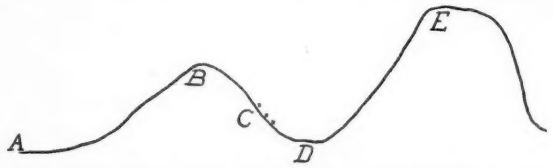
(1) The almost absolute certainty of securing satisfactory results when a scientific man or a farmer uses it for experimental or practical purposes.

(2) The wonderful influence it has had upon the development of the beet-sugar industry in Germany and other parts of the world.

[1] Read before the New York Section of the American Chemical Society, February 10, 1899.

Its action upon vegetation is so certain and so uniform, and the demand of crops for additional supplies of it in the soil is so universal, that an experiment station can scarcely mistake in recommending the use of sodium nitrate, where the conditions affecting the production of bountiful crops are obscure. It is probably the most stimulating fertilizer in the market, and while the most satisfactory results can be obtained from it when in combination with ample supplies of available phosphoric acid and potash, which if not already found in the soil, should be applied to it in order to secure most bountiful harvests, yet as a special fertilizer a moderate application of nitrate alone, on most soils, proves highly remunerative.

At present, the entire supply of sodium nitrate comes from Chili, although it is found in some other parts of the world, but not in sufficient quantities to compete in the markets of the world. The portion of the west coast of Chili, where it is found, between latitudes 19°12′ south, and 25°45′ south, extends over a length of approximately 260 geographical miles. The principal deposits are found in the provinces of Tarapaca and Antofagasta, in Chili, and the center of trade is Iquique. It exists in a long, narrow strip, averaging about two and one-half miles in width, extending along the eastern slope of the Coast Range, at an average distance of perhaps fourteen miles from the ocean, but in a number of cases it is probably as much as forty miles from the coast. The region where it is found is a rainless desert, absolutely devoid of vegetation. The nitrate beds exist at a height of from 3,000 to 5,000 feet above sea-level, and extend down towards the valley of Tamagruel. The following rough sketch, not drawn to scale, will serve to illustrate the characteristic surface of the portion of Chili where the *caliche* is found. It will be seen that it lies between the Coast Range and the Cordillera.



A = Pacific Ocean; B = Coast Range of Mountains; C = Location of *Caliche* Beds; D = Valley of Tamagruel; E = Cordillera.

I cannot undertake the discussion of all of the theories in regard to the origin of these beds, but suffice it to say that the most satisfactory explanation seems to be that they have resulted from the decay of enormous quantities of organic matter particularly seaweed which probably accumulated in a long, narrow strip of water, somewhat like Core Sound on the coast of North Carolina.

This accumulation, in the course of ages, was elevated. One of the evidences of this lies in the fact that the remains of seaweed are found in the nitrate deposits. The beds are 500 or 600 feet above the valley of Tamagruel, and extend down toward it, decreasing in value as they approach it, until they finally disappear upon reaching it. The beds exist under the following conditions, and skilled prospectors can generally locate the beds with considerable certainty by the surface indications:

The surface for a depth of approximately ten inches is covered with a layer of fine, loose sand; under the sand is found a layer of amorphous porphyry, feldspar, sodium chloride, and other mineral matter, cemented together by gypsum into a compact mass varying in thickness from six to ten feet. This is called *costra* or crust. Under this crust is found the *caliche*, or impure sodium nitrate, varying in thickness from a foot and a half up to about twelve feet. The *caliche* occurs in a great variety of colors, as yellowish white, orange, blue-gray, and dirt color. This deposit is a regular stratum, with all the appearances of a rock formation, firmly cemented together, and is displaced from its natural position, by blasting. The system of blasting is peculiar in this, that they drill a hole through the crust and through the *caliche*, down to the clay surface beneath, large enough to admit a boy, who is let down and excavates the clay under the *caliche*, so that the blast can be placed under the material to be broken up, the object being to thrust up as large a mass of *caliche* as possible. This is then broken up by the tools of the workmen into chunks the size of an orange, and the impurities as carefully removed by the process of selection, as possible. This crude material is then transported to the works where it is run through a crusher, and dissolved in hot water. The better quality of *caliche* contains from forty to fifty per cent. of sodium nitrate. The average quality from thirty to forty per cent. of sodium nitrate, and the poorest quality that is worked, from seventeen to thirty per cent. of sodium nitrate. The best quality of *caliche* runs about as follows:

	Per cent.
Sodium nitrate	50
Sodium chloride	26
Sodium sulphate	6
Magnesium sulphate	3
Insoluble	14
Sodium iodate, Sodium nitrite, Magnesium chloride, Potassium chloride, Magnesium nitrate	1
	100

Under the present depressed condition of the industry, it is not profitable to mine *caliche* with less than about thirty per

cent. of nitrate. The refining of *caliche* and the extraction of the sodium nitrate, depends upon the fact that sodium nitrate is very much more soluble in hot water than in cold water, while the solubility of salt in water, is little increased with increased temperature. However, the solubility of the nitrate in water at 20° C. is affected by a solution of salt, and while 100 parts of water, at 20° C., should dissolve 88 parts of sodium nitrate, when it contains 25 parts of sodium chloride in solution, it will dissolve only 52.8 parts of sodium nitrate.

The time at my command does not permit me to go into the details of the three systems in use in carrying out the solution, crystallization, and drying of the sodium nitrate. The crystallized sodium nitrate is removed from the mother-liquor and allowed to drain some time, after which it is put into sacks, where it drains still further, for a certain length of time, and the granulated appearance of the sacks as they come into our market is due to the crystallization of this drainage material upon the outside of the sacks.

The mother-liquor, from which the first crop of crystals is taken, can be used for dissolving a fresh supply of *caliche*, but it is not practicable to use it more than twice or three times. This mother-liquor which contains the impurities of sodium nitrate is worked over for the iodine contained in it. In fact, all of the iodine in the market at present, is produced as a by-product in the refining process of sodium nitrate, and could be thrown upon the market in such large quantities, that the price of iodine would be reduced to a very much lower figure, were it not for the fact that it is under the control of a combination, which regulates the output.

There is another product that might be secured, if some one could devise a profitable and sure method of manipulating it, and that is the sodium perchlorate. In some of the mines an appreciable percentage of sodium perchlorate is found mixed with the nitrate, and the chemist who can devise some cheap and effective means of extracting the perchlorate, will undoubtedly find it a very profitable discovery, as its presence is highly objectionable when found in the sodium nitrate, whether it be used as a fertilizer or for technical purposes.

There are two grades of sodium nitrate in the market: One grade, containing not less than ninety-six per cent. of sodium nitrate, or over sixteen per cent. of nitrogen, is imported for technical purposes,—manufacture of chemicals, and chemical industries. Then there is the second grade, called ninety-five per cent. nitrate, which contains not less than fifteen per cent. of nitrogen, imported more especially for fertilizer purposes. The sodium nitrate as it comes into this country is of very uniform composition and can generally be relied upon to analyze very

close to the figures given. It generally contains from one per cent. to two per cent. sodium chloride, which is largely due to the difficulty of crystallizing out the sodium nitrate on a large scale without also securing a little of its impurities. Where it is desired to have purer nitrate than is produced at the works, it should be recrystallized.

Sodium nitrate is used

(1) As a special fertilizer.
(2) In compounding complete fertilizers.
(3) In the manufacture of sulphuric acid.
(4) In the manufacture of nitric acid.
(5) In the manufacture of nitrate of potash.
(6) In the manufacture of arseniate of soda.
(7) In the manufacture of fireworks.
(8) In the manufacture of fusing mixtures.
(9) In the purification of caustic soda.
(10) In the manufacture of steel.
(11) In the manufacture of glass.
(12) In the manufacture of minium.
(13) In the curing of meat.
(14) For making chlorine in the manufacture of bleaching-powders.

From the above list of the uses to which sodium nitrate is put, it will be seen at once that it plays a very important part in the industrial development of the country, and the question naturally comes up, "How long will the available supply last?" As I showed above, the consumption amounts to approximately 1,000,000 tons a year. There are at present exploited in Chili, beds of *caliche* estimated by different geologists to contain from 63,000,000 to 120,000,000 of tons of nitrate, and it seems that only a very small proportion of the territory where nitrate is likely to be found has yet been exploited, so that we need have no fear of the supply giving out during the next generation.

I have devoted considerable time to a review of facts, some of which are doubtless familiar to all of you, but all of which are probably not familiar to all chemists and are not readily accessible to many. Its use as a fertilizer, as it becomes known, will undoubtedly extend very widely. At present prices, it is perhaps the cheapest source of nitrogen in our markets.

But I must now turn my attention to another phase of the question, which is forced upon us by the rôle that sodium nitrate plays in agriculture. Agricultural chemists in particular have been laboring for years upon the problem of furnishing some cheap, natural means of producing nitrate rapidly, and in season for agricultural uses. It has been demonstrated beyond the shadow of a doubt that the majority of agricultural crops

appropriate their nitrogen in the form of nitrates, a few being able to utilize it to a limited extent in the form of ammonia or humate of ammonia, and still others being able to secure their nitrogen supply by the action of micro-organisms which develop tubercles upon their roots, and enable them in this way to appropriate supplies of nitrogen which may be secured from the air or from nitrogenous compounds decomposing in the soil. There has sprung up, in connection with the study of these problems, almost a new branch of chemistry; that is, the study of the chemical reactions evolved by microscopic life.

Stutzer and Hartleb have shown that all cultivated plants, with the probable exception of the leguminosæ, appropriate their food in the form of nitrates, which are derived either from the fertilizers applied to the land, or from the nitrogenous substances in the soil which are converted into nitrates by the action of nitrifying bacteria. It has not yet been shown exactly in what form the nitrogen, appropriated by the leguminosæ through the bacteria existing in the tubercles upon their roots, is finally appropriated by the plant. It is, however, certain that the tubercles upon plants of this class are not able to appropriate the nitrogen from nitrates more freely, if indeed as freely, as they can from the free nitrogen of the air or soil. These tubercles upon the roots are the laboratories of the plant, apparently for the purpose of transforming the nitrogen of the air into suitable plant food for that class of plants. It is also quite well established by numerous investigators that the micro-organisms found in these tubercles have the power of producing within the soil where the plants grow, a capacity for storing up nitrogen, either in the roots of the plants themselves, or in the soil immediately surrounding them, in a form which can be appropriated as plant food by succeeding crops. Thus, crops of clover or peas, beans, vetches, serradella, lupines, and similar plants, apparently cause an accumulation of available nitrogen in the soil where they grow. The amount of this nitrogen accumulated from year to year is not large, but is sufficient to produce a perceptible effect upon the succeeding crop, and if it were possible by this means to continue indefinitely the growth of crops of this character upon the same land, it might be possible to fertilize the land by means of clover, peas, or other green manures of this character up to the point where maximum crops could be secured without the addition of fertilizers from other sources. These crops (especially clover) are looked upon with much favor in sections of our country where extensive farming, in contradistinction to intensive farming, is largely pursued. Not only do these crops, whether in the form of green manures plowed under, or simply as nitrogen storers, accumulate nitrogen within limited margins, but they also improve the physical condition of the soil, so as to

enable the succeeding crops to more readily secure plant food existing in the soils. The importance of these nitrogen storers to the development of agriculture cannot therefore be overlooked, but as it is not evident that they derive their nitrogen from, or convert it into, any form of nitrate before the plant appropriates it, I will not enter further into the discussion of their use.

Hellriegel and Wilfarth found that certain soils would not produce satisfactory crops of these nitrogen gatherers unless they had been derived from fields where these crops had been grown, even when provided with abundant supplies of nitrogen in the form of organic compounds, or of nitrate. These pots, however, could be made to produce luxuriant growths of these nitrogen gatherers, if watered with the extract of the soil where the plants had grown. If the plants were watered with the sterilized solution of the soil, no growth was produced. The same pots, however, would produce a growth when watered with the unsterilized solution of the soil.

Nobbe went one step further, and reasoned that these unfruitful soils could be made fruitful if inoculated with the micro-organisms existing in, and probably producing, the tubercles. His experimental work was carried out with a view of determining the truth or falsity of this hypothesis. Operating upon sterilized soils containing ample supplies of available plant food, he found that his nitrogen gatherers would not grow beyond the point where they derived their supplies of nitrogen from the seed in sterilized soil, and that no tubercles were developed upon the roots of these plants. If, however, the soil was treated with a solution of pure culture of the bacteria existing in the tubercles, it immediately became fruitful and developed plants with abundant root tubercles. He found further that while the pure cultures indicated that the micro-organisms existing in the tubercles of the various nitrogen growers appeared to be the same under the microscope, yet they were not capable, except in a minor degree, of producing tubercles upon other members of the leguminosæ. For example :

The pure culture derived from the tubercles of the pea would produce tubercles upon the different varieties of peas, but might have little or no effect upon beans, or upon clover. So that he arrived at the conclusion that each plant had its particular class of micro-organisms capable of producing ample supplies of tubercles upon the roots of its own or closely related species, but incapable of producing tubercles upon plants remotely related to it. In connection with carrying out this idea in its practical applications, he set to work to prepare pure cultures of the organisms characteristic of the above plants, and a company has been organized in Germany for the preparation of these pure cultures upon a commercial scale. The medium employed is agar-

gelatine. This is inoculated with the germs derived from the tubercles of the clover, the lupine, the pea, etc., as may be required, and is furnished under the name of *Nitragin* for the inoculation of soils with proper germs for the production of the desired crop.

The inoculation of the soil with these germs is effected in two ways:

(1) By moistening the seed with a solution of the inoculated agar-gelatine.

(2) By moistening dust or fine earth with a solution of inoculated agar-gelatine, and working it into the soil.

Probably the best results have been obtained from the latter process.

It has been found, experimentally, that soils which would not produce particular crops of these nitrogen gatherers before inoculation, could, in some cases, be made to produce fair crops by the inoculation. As a scientific curiosity it is of great value. In practice, however, it has failed to yield satisfactory results, and the time does not yet seem to have arrived when this system can be economically applied by the farmer. It should be remembered, also, that this principle applies only to the nitrogen gatherers, or plants deriving their nitrogen supply through tubercles. It costs about two dollars an acre to properly inoculate a field with the organisms necessary to produce any particular kind of leguminous plant. The uncertainty of the inoculation proving successful is so great, that Prof. Paul Wagner, Director of the Darmstadt Experiment Station, Germany, recommends the farmers of that country not to attempt it.[1]

Caron-Ellenbach has gone one step farther than the above, and has attempted to increase the capacity of the soil for directly absorbing nitrogen from the air. He has isolated and produced the pure culture of an organism which he has christened *Bacillus-Ellenbachensis* α which he finds possesses, in high degree, the power of causing the soil to absorb atmospheric nitrogen and transform it into available plant food. His claim is that soil inoculated with this bacterium increases its capacity for yielding up nitrogen in an available form for cereals and other crops, and that it absorbs large quantities of nitrogen from the air, and produces ample supplies for the use of the plants without resorting to expensive commercial fertilizers. The pure culture of this bacterium is also manufactured on a commercial scale by a firm at Elberfeld, Germany, and is sold under the name of *Alinit*. This preparation, like *Nitragin*, has in practice been found to be a scientific curiosity, but while *Nitragin* has considerable experimental evidence to show that it frequently may

[1] The most successful work done in this country upon this subject is by J. F. Duggar, Ala. Exper. Station Bull. No. 87.

increase the production of the leguminosæ, there is not, so far as I have been able to discover, any appreciable amount of scientific evidence to substantiate the claims set up for *Alinit.* In fact the *Bacillus-Ellenbachensis α* seems to be such a delicate creature, that the probability of its ever attaining any prominence in increasing the world's production of cereals, is relegated to the distant future.

While both of these discoveries are of great scientific interest, neither of them, I think, can be considered as anything more than demonstrating the fact that scientific men are working along very close to the lines where scientific discoveries of great practical value might be made.

Could the result sought to be attained above, be successfully and economically accomplished, the perplexing nitrogen problem would be solved for the farmers, but as they have not accomplished the results, it is necessary for scientific men to look further. The most promising field at present seems to me to be the study of the soil conditions which promote the rapid formation of nitrates, because that is the objective point to which we must direct all of our energies before we can expect to have any fertilizer, or any source of nitrogen supply utilized by the plant. We may have present in the soil, an abundant supply of nitrogen, and yet the plant may starve to death for nitrogen, because it exists in an unavailable form and cannot be converted into available form in time for the plant to utilize it.

The meteorological conditions most favorable to the production of nitrates are quite well known. But these we cannot control. It is demonstrated that there is a continual change going on in the supplies of nitrates present in the soil. They are carried down by the heavy rains, and they rise to the surface as the soil dries, so that there is a continuous movement of them in the soil. If the supply is ample, it is shown by a dark-green, luxuriant growth of vegetation. If it is inadequate, it is indicated by a stunted growth, and a yellowish-green color. The experimenter, therefore, is always in a position to determine, approximately, whether his plants are securing a sufficient supply of nitrates.

Until comparatively recently, the methods of analysis for detecting nitrates were not sufficiently delicate to throw full light upon the problem. Since, however, it has been discovered that the sulphate of diphenylamine is a sufficiently delicate test for nitrate to indicate one part in 100,000,000, it has been possible to shed much light upon the movements of nitrates, and the existence of nitrates in agricultural plants. Serno has found nitrates in almost all families of plants. The largest quantities occur in Malvaceae, Cruciferae, Papervaceae, Convolvulaceae, Labiatae, Compositae, and Urticaceae. In many plants it occurs

only in the roots, and more especially only in the newly formed, absorbing roots. He finds that it is stored in the roots during the winter in some; in others it is found only in the spring. In annuals the nitrates occur abundantly in all parts.

Deherain has found that wheat will store as much as one per cent. of nitrates in the roots of the plant during the winter time, and that if the dry roots be dipped in a solution of the sulphate of diphenylamine, they take on a deep blue color, indicating the presence of a very large percentage of nitrates retained in the roots preparatory for use when growth starts in the spring. Damussy has found that these nitrates are not washed out from the roots by cold water, although they are readily extracted by warm water, or when the roots are subjected for some time to an atmosphere of chloroform and then washed with cold water. This, he thinks, indicates that the nitrates are held in the roots in some very unstable compound, perhaps with the protoplasm, and resume their normal condition whenever the protoplasm is modified by an elevated temperature, or by chloroform.

Serno is of the opinion that nitrates stored in the roots of plants during the winter, which, as growth begins in the spring, may be traced into the stems of the plants as they move up to the leaves and finally lose their identity in the leaves, are converted by the changes taking place in the growing plant, into some form of amides, especially, perhaps, asparagine. Our methods of analysis, however, are not sufficiently perfected to trace these compounds exactly to the point where this change takes place. They can be followed up the plant in the spring, quite distinctly in the roots, less distinctly in the stem, and they gradually disappear as they rise. This principle applies to a very large number of agricultural plants, and the power of these plants to store up nitrates in their roots is of great advantage in keeping a supply of available nitrogenous plant food within reach, which would otherwise have been washed out of the soil by the fall and winter rains. It is familiar to all of us that the nitrates form in greatest quantities during the moist, warm summer months, and that they exist in the soil in largest proportions in the latter part of the summer. This storing capacity of plants therefore is of great importance.

S. Winogradsky has devoted a large amount of time and attention to the study of the nitrifying organisms which convert ammonia salts into nitrates. He began by operating upon the soils around Zurich, and has extended his investigation to cover samples of soil taken from many countries of the world and from all climates. He has succeeded in isolating and preparing the pure culture of a group of organisms, called by him 'nitromonas,' which he is disposed to consider rather as a group of bacteria than as a single species whose special function is the

oxidation of ammonia. He had already isolated bacteria whose special function was the oxidation of sulphur compounds and also the oxidation of iron compounds, which he named respectively 'sulfo-bacteria' and 'ferro-bacteria.' He therefore named these producing nitrate, 'nitro-bacteria.' He found that the nitromonas secured from different parts of the world possessed varying degrees of intensity of action. In the pure cultures, those from Europe acted slowly, and after a few generations of pure cultures, lost the power of oxidizing ammonia salts, while those secured from the soils of South America and Africa attacked the ammonia salts with great energy and seemed to acquire greater activity with successive generations. He has done an immense amount of work in the study of these bacteria, and has shed much light upon the peculiarities of their actions.

He also found that the nitromonas developed normally either in the light or darkness, and that they can assimilate the carbon from carbon dioxide in entire darkness. They are able, in entire darkness, to appropriate this carbon from carbonates or from carbon dioxide, and cause it to combine with the nitrogen to form organic matter, without the aid of the sun's rays. He believes that some sort of an amido compound is produced at the expense of the carbon dioxide and the ammonia. These chemical changes developed by the nitromonas, differ materially from those which occur with chlorophyl. In the action of chlorophyl, carbon dioxide is decomposed by the sun's rays, the oxygen liberated, and the carbon unites with the hydrogen and oxygen to form carbohydrates, but the investigations of Winogradsky indicate that the nitro-bacteria, instead of decomposing the carbon dioxide and setting oxygen free, effects its union with ammonia and makes use of the oxygen of the air to oxidize the nitrogen to nitrous and nitric acids, the energy for this change being supplied to them from the oxidation which they bring about. At this point there is room for still further investigation which, I believe, Winogradsky is engaged upon.

The conditions favorable to the oxidation of nitrogen compounds to nitrous and nitric acids, by the respective nitrifying organisms whose special function is to bring about these changes, have been studied extensively by Warrington, Schlösing, Winogradsky, and others, and the conditions favorable to the production of nitrates in the soil are quite thoroughly understood, and if we were able to control the meteorological conditions, it would perhaps not be a difficult matter to develop in the soil a very large quantity of nitrates suitable for plant food. As we are unable, however, to control the meteorological conditions, the best that can be done is to see that the soil is properly drained, properly cultivated, and supplied with a sufficient quantity of

lime or other alkali, to prevent the acidity from interfering with the regular processes of nitrification.

Even with this, however, it has been shown by E. Breal that there may be an extensive destruction of nitrates by the action of an antagonistic bacterium or ferment, which he finds developing extensively, especially upon straw and other vegetable refuse. This ferment has the power of attacking the nitrates and liberating the nitrogen as free nitrogen. It has long since been shown that putrescent fermentation reduces nitrates to the lower oxides and finally to ammonia. This ferment, however, acts differently in that it does not reduce the nitrates to lower oxides, but sets the nitrogen free. In one case, one-third of the nitric acid under experimentation disappeared: in another, sixty-seven per cent. of the nitric nitrogen disappeared. The rapidity of the decomposition has been measured and the products of decomposition analyzed. He has shown that when the soil containing nitrates is drying, and the nitrates rising, if covered with wet straw or other vegetable refuse and allowed to dry out slowly, nitrates are not found either in the straw or surface soil. This condition, in his judgment, accounts for the failure to find nitrates in meadows, forests, or other lands strown with large amounts of vegetable refuse, a fact which was also noticed by Boussingault. It also accounts, probably, for a large amount of the loss of nitrogen which occurs when green manures are used. It is a notorious fact that a large percentage of the nitrogen stored in a crop used as a green manure seems to escape, and the discovery of this ferment by Breal probably accounts for it. We are therefore confronted by these difficulties in the production of nitrates in the soil:

(1) The reduction of nitrates by putrefactive fermentation.

(2) By the action of Breal's bacterium.

So that it seems not to be possible to produce in a soil under normal conditions, more than a very small percentage of nitrate, and rarely enough to answer the maximum requirements of a large crop.

Time will not permit me to notice the work of all of the investigators who have contributed to extend our knowledge of the activity and peculiarities of the bacteria which perform so much work for the benefit of agriculture. There is one more investigation which I wish to notice, and I am through. It is well known that there is great diversity in what is known as the availability of nitrogen in its various forms when used in compounding fertilizers, or when used as a direct fertilizer upon the land. This variation in availability is dependent upon the readiness with which the nitrogen compound, whether it be ammonia salts or vegetable or animal refuse, is converted into nitrates.

Recently, S. W. Johnson, E. H. Jenkins, and W. E. Britton, of the Connecticut Experiment Station, undertook an investigation to determine the availability of a number of the chief sources of nitrogen, used for compounding our commercial fertilizers. They used for this purpose, oats, Hungarian grass, and rye. The soil upon which the experiments were conducted was quite thoroughly exhausted by previous crops, and ordinary precautions to prevent errors creeping in were observed. They determined the percentage of available nitrogen in different sources of nitrogen, as shown by the plants indicated in pot experiments, as follows:

	Per cent.
Sodium nitrate	100.0
Dried blood	73.3
Dried fish	93.9
Ground bones	16.7
Tankage	49.4
Horn and hoof powder	63.3
Linseed meal	68.9
Cottonseed meal	64.8
Castor pumice	64.6

It will be noticed in this experiment, as is now generally the case, that sodium nitrate is taken as the standard of availability.

There is one other possible source of nitrate that may become available, and that is the nitrate that is developed by the action of electricity upon the nitrogen of the air and certain chemicals or minerals. This has not yet developed to be of economic importance, and while in the opinion of some eminent scientific men, the time may not be far distant when we may economically produce nitrate by electricity, we have not yet reached that point.

At the request of our president, I have compiled this review of the present state of our knowledge of the nitrate problem. I could not, without occupying too much of your time, go into the details of many other laborious investigations, carried on in many countries by careful and patient scientific men. What I have said is classified as follows:

(1) The sodium nitrate is the most important source from which available nitrogen can be supplied, at the present time. I have given you some account of the sources of supply, and the character and uses of the finished product as it comes into the market.

(2) The rôle that nitrate plays in agriculture.

(3) The efforts of scientific men to provide it, or furnish a substitute for it.

(4) Scientific investigations bearing upon it, showing at considerable length the important relations of bacterial life to its production and destruction.

In conclusion, I may say that science has failed, so far, to provide a substitute for the natural nitrate, and it is more economical to avail ourselves of the reserve supplies, representing the accumulated work of bacterial ferments during protracted geological periods of the past, in the now desert regions of Chili, than it is to rely upon their inadequate and uncertain work in our soils under the unfavorable natural conditions prevailing in our climate. JOHN A. MYERS.

NOTES.

On a Possible Error in the Determination of Nitrogen in Nitrates Due to Impurities in Reduced Iron.—Reduced iron is employed in two of the methods for the determination of nitrogen in nitrates, which are in use by the Association of Official Agricultural Chemists. Recently, in making blank determinations with a new lot of so-called chemically pure reduced iron it was found that, by the modified Ulsch method, much less ammonia was required for neutralizing the acid than in the case of blank tests formerly made. The error from this cause in determinations involving half a gram of commercial sodium nitrate, would amount to from 0.30 to 0.35 of a per cent. By direct distillation, without first allowing the iron to dissolve in the acid, no difficulty was experienced. The reduced iron bore the label of one of the leading manufacturers of chemicals in Germany and was ordered through a prominent and reliable firm in this country.

Since these tests were made, an account of a similar observation by L. Brandt[1] has been noticed. Brandt found in a similar manner an error equal to eight-tenths of a per cent., assuming half a gram of nitrate to be employed in a single test. As in our own case, he assured himself that the error was not due to any of the other reagents, nor to the apparatus employed and also found that the error did not appear unless the iron was dissolved in the acid before the distillation. From various tests made by Brandt, he concluded that the impurity in the iron was in the form of some organic nitrogen compound, which probably gained access to it, subsequent to its reduction by hydrogen. Further experiments showed that the impurity could be removed by heating the iron in a current of hydrogen, though the accom-

[1] *Chem. Ztg.*, 23, 22 (*1899*).

plishment of the object was impossible by extraction with water, alcohol, or ether. Brandt very properly closes the account of his observations by stating that the experience further indicates the propriety of never placing implicit confidence in chemicals claimed to be chemically pure, but to test everything before using it.

In view of the recent extension of the use of the modified Ulsch method in the laboratories of this country, it seemed important that our own analysts should be put on their guard as to the possible character of the reduced iron sold as chemically pure. B. L. HARTWELL AND H. J. WHEELER.

On the Determination of Sulphur in Sulphites.—This method is founded on the following well-known reaction: Sulphur dioxide, when brought into contact with nascent oxygen and water, is transformed into sulphuric acid. The operation is conducted as follows: The weighed sulphite dissolved in water is placed in a beaker, and a mixture of water, hydrochloric acid, hydrogen peroxide, and barium chloride is added in sufficient quantity. The beaker is covered with a watch-glass, gently heated, and the operation conducted as in the case of a determination of sulphuric acid.

$$\text{Weight of } BaSO_4 \times 0.1371 = S.$$
$$\text{Weight of } BaSO_4 \times 0.2742 = SO_2.$$

The reaction comprises three phases:

(1) The sulphite is decomposed by hydrochloric acid, which liberates sulphurous acid.

(2) Sulphurous acid decomposes hydrogen peroxide and unites with the nascent oxygen forming sulphuric acid.

(3) Sulphuric acid with barium chloride gives barium sulphate.

Potassium metasulphite, $K_2S_2O_5$, analyzed by this method has given:

	Calculated. Per cent.	Found. Per cent.
Sulphur	28.8	28.8560
Potassium	35.1	34.9755
Oxygen	36.1	.....

In using the bromine method the result for sulphur was 29.0202 per cent.

Commercial hydrogen peroxide cannot be employed, as it generally contains sulphuric acid. A proper reagent for this purpose is obtained by adding hydrated barium dioxide to water acidulated with hydrochloric acid.[1] The barium dioxide is added in small quantities until the liquid is alkaline, when alumina and ferric oxide are separated. The turbid alkaline liquid is thrown on a pleated filter and the filtrate collected in a vessel containing some hydrochloric acid. This filtrate is then ready for use.

A. BOURGOUGNON.

Fuller's Earth.—A recent discovery of a large deposit of fuller's earth in Florida promises to be of considerable importance to the oil trade. Up to the present all the fuller's earth used by the cotton oil, and lard manufacturers has had to be imported from England and has sold for as much as $15 to $20 per ton in New York. The domestic product has so far proved unsuitable for this particular purpose and has sold for only $7 per ton, and is used only in the mineral oil industry. The product from this newly discovered deposit has been thoroughly tested by experts in the cotton oil industry and is pronounced to be fully equal to the best grades of the imported material. So soon as capital can be interested in the property the consumers will be able to obtain a high-grade fuller's earth of domestic origin which will cost them very much less than they at present have to pay. The terms on which the property is offered are so favorable that the new material will no doubt soon be put on the market.

F. T. SCHREIBER.

NEW BOOKS.

THE OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D. New York: The Macmillan Co. 1898. xx + 541 pp. Price, $3.50.

While no book can fully cover a field so rich in carefully guarded secrets as those pertaining to technical chemistry, I know of no treatise on that subject which gives the student a clearer and more comprehensive view thereof than Thorp's "Outlines of Industrial Chemistry."

The student who has mastered its contents can visit a factory

[1] This Journal, 12, No 3 (*1890*).

and, notwithstanding the usual habit of rushing the visitor through the place as quickly as possible, can understand the *modus operandi* more fully than the guide has reason to expect.

Teachers may congratulate themselves upon the appearance of this book, for it contains, expressed in a concise manner, much that would otherwise (with perhaps less happy results) require the consultation of many books.

In a work so thorough it is difficult to select any one subject more carefully treated than the others; therefore, chemists can well feel grateful to Prof. Thorp for his contribution and doubtless few libraries will be without a copy thereof.

ALFRED SPRINGER.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW, AND GREASE FOR LUBRICATION, ETC. By an expert oil refiner. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. Price, $3.50.

This book purports to give "to merchants and manufacturers in the different branches of these trades practical hints for the compounding of oils, also for the utilization of waste products, such as ullages, etc," and treats chiefly of lubricating oils, with one chapter on lamp oils.

Numerous receipts are given for compounding these oils for various uses with some hints and cautions. The flash and viscosity tests of mineral oils are described and also some of the simpler tests of animal and vegetable oils for the purpose of detecting adulteration. The real character of the various mixtures given and the reason of their usefulness for particular purposes seems to be ignored. So also the general theory of lubrication.

While to one entirely ignorant of the subject such a work would give an idea of the combinations of mineral and fatty oils which have been found useful for lubrication, it is difficult to see how the intelligent manufacturer will be benefited by so superficial a treatise.

E. TWITCHELL.

LIGHTING BY ACETYLENE. GENERATORS, BURNERS, AND ELECTRIC FURNACES. BY WM. E. GIBBS, M.E. Second Edition, Revised and Enlarged. New York: D. Van Nostrand Co.; London: Crosby, Lockwood & Son. pp. 161. Illustrated. 1899. Price, $1.50.

Mention was recently made in these pages of the first edition

of this work, and the present edition calls for little further notice. The author has added some twenty pages on the subject of generators, and has somewhat expanded the chapter on "Generation of Acetylene"; otherwise the volume is little changed.

A misplaced decimal point on p. 37 makes the theoretical yield of acetylene from 100 pounds of carbide 5.81 instead of 581 cubic feet. The author confuses benzine with benzene, referring to the former as a polymer of acetylene. The limits between which acetylene forms an explosive mixture with air are much greater than those stated by the author. The figures given apply more nearly to ordinary coal-gas. E. G. LOVE.

LAVAS AND SOILS OF THE HAWAIIAN ISLANDS. By WALTER MAXWELL, Director and Chief Chemist of the Experiment Station of the Hawaiian Islands. 186 pp.

The work is an important contribution, perhaps the only contribution, to our knowledge, of the composition of the soil of the islands, which have lately come into the dominion of the United States. The total area of the islands where agriculture is possible is 6,740 square miles. The islands of the Hawaiian group are of pure volcanic origin. Fifteen volcanoes of the first class have existed at different times and been in action in the islands. The group of islands therefore represents a portion of the great mass of matter due to volcanic action, which has been projected above the water's level. The composition of the soil is, therefore, what would be expected from the decomposition of basaltic lavas. In type the soils differ from those of our country in being essentially basic instead of acidic. In the ordinary soils of the United States the acidic element, namely, silicic acid, is the predominating factor, while in Hawaiian soils, lime, alumina, and iron make up almost, if not quite, half of the total weight of the soil.

In the decay of these lavas, in the activity of the usual forces which produce the disintegration of rocks, the functions of water, steam, and air have been extremely prominent. In addition to this the vapors of sulphuric acid, which find their way by means of the steam into the crevices and broken surfaces of the lava masses, has added greatly to the power of water and steam in disintegrating the rock masses. In one instance where a quantity of steam was condensed and preserved for analysis, it was

found to contain 4.92 per cent. of sulphuric acid. The steam contains practically no chlorine, which leads to the belief that the sea-waters do not penetrate into the depths whence the heat of the volcanoes comes.

Two distinct types of soils have arisen from the decay of these volcanic lavas. These are distinguished chiefly by their color and are known as the "yellow" and "red soils." In regard to fertility the dark red soils are much more productive than the light red or yellow soils.

The Hawaiian soils are remarkably rich in phosphoric acid and in iron, about twenty-five per cent. of the weight of the soil consisting of iron oxide. Thus it is seen that the silica of American soils is largely replaced by the iron and aluminum of Hawaiian soils.

The chief agricultural crop of the Hawaiian Islands, as is well known, is sugar, and there is no country in the world where so great a quantity of sugar can be grown per acre. In general, it requires two years to produce one crop, inasmuch as the crop is allowed to grow about eighteen months, and the other six months are consumed in harvesting, preparing the lands, and replanting.

The average yield of sugar, per acre, for the "dark red soils" is a little over 10,000 pounds, and for the "yellow soils" a little over 6,000 pounds. Very much larger yields are occasionally reported; namely, from 20,000 to 25,000 pounds per acre in some instances.

In the methods of analysis for determining the available plant food in soils, Dr. Maxwell has introduced an interesting innovation. He has proposed the use of aspartic acid, as a solvent for the available plant food in soils; namely, the phosphoric acid and the potash.

In a comparison of the amount of plant food removed by successive cropping with sugar-cane and that removed by digestion with a one per cent. solution of aspartic acid for twenty-four hours, he has shown that in ten years of cropping practically the same quantity of plant food is removed, as in the digestion of the soil for twenty-four hours with a one per cent. solution of aspartic acid. He therefore proposes to measure the available plant food present in the soil by digesting with a one per cent. solu-

tion of aspartic acid for twenty-four hours and dividing by ten the quantity of phosphoric acid and potash obtained.

Under the conditions of rainfall, which prevail in the parts of the islands studied by Dr. Maxwell, he has found that the quantity of plant food removed by cropping is practically the same as that removed by the drainage waters.

The student of soil chemistry and physics as well as the practical farmer will derive much benefit by carefully reading Dr. Maxwell's pamphlet. H. W. WILEY.

TESTING MILK AND ITS PRODUCTS. By E. H. FARRINGTON AND F. W. WOLL. Fourth revised and enlarged edition. Madison, Wis.: Mendota Book Company. viii + 256 pp.

The general introduction of the Babcock method has been one of the most important aids to the producer of dairy products, and as a natural result, there has been a demand for a work which would enable one to understand and apply the processes connected with modern dairy practice. This demand has been met by the authors in an admirable little volume upon the subject which is now in its fourth edition. Consideration is given to the principles of the Babcock method, followed by many aids and apt suggestions in order that one may become familiar with the method and its application. The testing of milk is treated in a thorough manner and especially is the treatment of the methods for the determination of the acidity of milk and cream to be recommended. The chemical analysis of dairy products is a section of the work which is of interest to the chemist as well as to one who has not had the advantage of laboratory training. The appendix contains many useful tables and helpful suggestions on practical creamery work. A very complete index closes the volume. The volume, as a whole, is a helpful one, and should be in the hands of those interested in the application of improved methods in the dairy industry of the country.

J. B. WEEMS.

BOOKS RECEIVED.

Digestion Experiments. Bulletin No. 160. The North Carolina Agricultural Experiment Station, Raleigh, N. C. 20 pp.

Drinking Water—City, Town, and Rural Supplies. Bulletin No. 161. The North Carolina Agricultural Experiment Station, Raleigh, N. C. 20 pp.

Farmers' Bulletin No. 87 (Experiment Station Work, VIII), U. S. Department of Agriculture, Washington, D. C. Soil Moisture; Fertility of Soils; Clover Crops for Orchards; Cultivating vs. Cropping Orchards; Transplanting Trees; Fecundity of Swine; Food Value of Eggs; Starch from Sweet Potatoes; The Toad as a Friend of the Farmer. 1899. 32 pp.

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